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(71) Applicant: JAPAN SYNTHETIC RUBBER CO., LTD.

Tokyo 104 (JP)

(72) Inventors:

- Miyamoto, Tsuyoshi  
Yokohama-shi (JP)

• Kimura, Masayuki

Yokkaichi-shi (JP)

• Eguchi, Kazuhiro,

Tsuchiura Reikusaide Haitsu 511

Tsuchiura-shi (JP)

• Matsuki, Yasuo

Yokkaichi-shi (JP)

(74) Representative: Lamb, Martin John Carstairs

MARKS & CLERK,

57-60 Lincoln's Inn Fields

London WC2A 3LS (GB)

**(54) A process of producing a polyimide block copolymer**

(57) A polyamide-type copolymer, a process of producing the same and use of the same in a thin layer forming agent.

In order to provide a polyamide-type copolymer suitable for producing an alignment layer in an SBE type display element with high transparency, adhesion, pretilt angle etc, the present invention provides processes of producing a block copolymer type polyamic acid, a polyimide block copolymer, a polyimide-polyamic acid block copolymer and a liquid crystal alignment layer wherein, in separate steps, first and second prepolymers comprising polyamic acid prepolymers or polyamide prepolymers are prepared and subsequently reacted together, and if necessary, imidised.

The invention also provides a thin layer forming agent having a first polyimide-type block and a second polyimide-type block bonded to the first polyimide-type block and having a different structure from the first polyimide type block.

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## Description

This invention relates to a process of producing a polyimide-type copolymer, to a thin layer forming agent, to a liquid crystal alignment layer and to processes of producing a thin layer forming agent and a liquid crystal alignment layer. Specifically, this invention relates to processes of producing a block copolymer type polyamic acid, a polyimide block copolymer, and a polyimide-polyamic acid block copolymer; a thin layer forming agent comprised of a polyimide-type block copolymer and a liquid crystal alignment layer comprised of a polyimide block copolymer and the processes of producing them.

At present, so called TN (Twisted Nematic) type display elements with TN liquid crystal cells are known for liquid crystal display elements: a substrate with a transparent conductive layer is formed with a liquid crystal alignment layer made of polyimide and the like to for use in a liquid crystal display element. Two of the substrates are put together so that a nematic-type liquid crystal layer having positive dielectric anisotropy is formed in a sandwich structure; the major axis of the liquid crystal molecule is continuously twisted, from one substrate to the other substrate, by 90°.

The liquid crystal alignment in a TN type display element is normally aligned by rubbing the treated liquid crystal alignment layer.

Recently, the SBE (Super Twisted Birefringency Effect) type display element, which exceeds the TN type display element in contrast and visual properties, is being developed. The SBE type display element uses a liquid crystal in which a nematic type liquid crystal substance is blended with a chiral agent formed of an optically active substance and utilizes the Birefringency effect generated from the condition that substrates are continuously twisted until the angle between the major axis of the first substrate and that of the last substrate reaches 180° or more.

When, for example, an SBE type display element is produced using a liquid crystal alignment layer comprised of conventional polyimide, the pretilt angle of the liquid crystal molecule coming out on the liquid crystal alignment layer is so small that, for example, it cannot be 3° or more. As a result, it is difficult to continually twist the liquid crystal molecule at 180° or more between the substrates and the resulting liquid crystal display element cannot have the predetermined display function.

For this reason, a SBE type display element needs to use a liquid crystal alignment layer of oblique evaporation of silicon monoxide formed by evaporation to obtain a large pretilt angle in reality. However, this liquid crystal layer requires a complex process and does not suit mass production.

On the other hand, a TN type display element is also required to have a large pretilt angle to reduce display deficiencies due to the reversed tilt phenomena during cell driving.

Knowing the above background, to obtain a large pretilt angle such as 3° or more, a polyimide, that inherently has the properties to be a liquid crystal alignment layer itself, has been considered as a liquid crystal alignment layer material. The polyimide having a long - chain alkyl group or fluorine atoms, for example, has been tested.

In this technology, however, the polarity of the polyimide itself can be decreased due to such a specific atom or atom group, providing a liquid crystal alignment layer with poor adhesion to substrates. As a result, the liquid crystal alignment peels from the substrate by rubbing required for providing a liquid crystal alignability.

A liquid crystal alignment layer comprising polyimide is provided by using a solution obtained by dissolving a polyamic acid (a polyimide carboxylic acid) or a soluble polyimide into an appropriate organic solvent as a liquid crystal alignment layer forming agent. The solution is then applied to the surface of the substrate that constitutes a liquid crystal display element cell to obtain a polyimide thin layer. The thin layer is then aligned by rubbing treatment or the like to obtain a liquid crystal alignment layer.

A selected partial area of the liquid crystal alignment layer may be irradiated by, for example, ultra violet light to correct the alignment properties before or after an aligning treatment by, for example, rubbing: in the area, the pretilt angle can be, for example, narrowed compared to other areas. Within the area in which different pretilt angle regions coexist, a liquid crystal display element provides excellent quality with less viewing angle dependency; contrast is less depending on the viewing angle.

Presently, for a polyimide used as a material for a liquid crystal alignment layer forming agent, a variety of properties are required in respect of its applications, functions, and the producing process of a liquid crystal alignment layer, as follows:

- (1) to obtain excellent alignment properties in a crystal display element by providing a predetermined pretilt angle,
- (2) to obtain high durability to the aligning treatment, such as rubbing,
- (3) to obtain excellent applicability,
- (4) to obtain high transparency,
- (5) to obtain high voltage retention,
- (6) to have little flickering in the liquid crystal display element,
- (7) to obtain excellent preservation property,
- (8) to be able to execute highly efficient correction of alignment properties by irradiation.

A conventional polyimide, however, does not have well balanced properties as mentioned above; normally, a polyimide excellent in a specific property does not have another specific property.

To obtain a polyimide having plural properties, a plural polyimide mixture having different properties may be considered; however, in this case, it is rare that these properties can be obtained together, but rather, differences in physical properties of each polyimide and insufficient miscibility make it difficult to obtain excellent properties, such as a high transparency, prerequisite for a liquid crystal alignment layer and sufficiently excellent applicability. As a result, the goal is not achievable.

A polyimide is produced by a polycondensation reaction between a tetracarboxylic dianhydride component and a diamine component or a diisocyanate component. To obtain a polyimide having plural different properties or a polyimide having denatured properties, several different a diamine component, for example, can be used for production together.

By such a process, however, it is difficult to control polycondensation reaction conditions and the predetermined polyimide cannot be obtained easily.

The invention was accomplished based on the prior art mentioned above. One of the objectives of this invention is to provide a polyimide-type copolymer which is useful, especially as a liquid crystal alignment layer material, providing predetermined plural properties. These properties are difficult to obtain at the same time by conventional methods.

Another objective of this invention is to provide a process of producing certainly and easily a block copolymer type polyamic acid, a polyimide block copolymer or a polyimide-polyamic acid block copolymer which provide the predetermined plural properties.

Another objective of this invention is to provide a thin layer forming agent to form a thin layer having excellent predetermined plural properties which are difficult to obtain at the same time by conventional methods and to provide a liquid crystal alignment layer having plural excellent properties which is difficult to obtain at the same time by conventional methods and the production processes of the liquid crystal alignment layer above mentioned.

The present invention provides a process of producing a block copolymer type polyamic acid, wherein a first polyamic acid block and a second polyamic acid block having a different structure from the first polyamic acid block are included in a molecule, the process comprising the following steps:

obtaining a first polyamic acid prepolymer having amino groups at its ends by a reaction between a tetracarboxylic component and a diamine component,

obtaining a second polyamic acid prepolymer having reactive groups at its ends originating from a tetracarboxylic component by a reaction between a tetracarboxylic component and a diamine component, and

reacting the first polyamic acid prepolymer with the second polyamic acid prepolymer.

Preferably a process of producing a polyimide block copolymer of this invention comprises the steps of imidizing a block copolymer type polyamic acid produced in the above mentioned process to obtain a polyimide block copolymer comprising a first polyimide block and a second polyimide block in the molecule.

The present invention further provides a process of producing a polyimide block copolymer, wherein a first polyimide block and a second polyimide block having a different structure from the first polyimide block are included in a molecule, the process comprising:

obtaining a first polyimide prepolymer having amino groups at its ends by a reaction between a tetracarboxylic component and a diamine component,

obtaining a second polyimide prepolymer having reactive groups originating from a tetracarboxylic component at its ends by a reaction between a tetracarboxylic dianhydride component and a diamine component, and

reacting the first polyimide prepolymer with the second polyimide prepolymer.

The present invention further provides a process of producing a polyimide block copolymer wherein a first polyimide block and a second polyimide block having a different structure from the first polyimide block are included in a molecule, the process comprising:

obtaining a first polyimide prepolymer having isocyanate groups at its ends by a reaction between a tetracarboxylic dianhydride component and a diisocyanate component,

obtaining a second polyimide prepolymer having carboxylic acid anhydride groups at its ends by a reaction between a tetracarboxylic dianhydride component and a diisocyanate component, and

reacting the first polyimide prepolymer with the second polyimide prepolymer.

The present invention further provides process of producing a polyimide-polyamic acid block copolymer wherein a polyimide block and a polyamic acid block are included in a molecule, the process comprising:

obtaining a polyimide prepolymer having carboxylic anhydride groups or isocyanate groups at its ends by a reaction between a tetracarboxylic dianhydride component and a diisocyanate component,

obtaining a polyamic acid prepolymer having amino groups or carboxylic anhydride groups at its ends by a reaction between a tetracarboxylic dianhydride component and a diamine component,

wherein a polyamic acid prepolymer having amino groups at its ends is used when the polyimide prepolymer contains carboxylic anhydride groups at its ends and

a polyamic acid prepolymer having carboxylic anhydride groups at its ends is used when the polyimide prepolymer contains isocyanate groups at its ends.

The present invention further provides a process of producing a polyimide-polyamic acid block copolymer wherein a polyimide block and a polyamic acid block are included in a molecule, the process comprising:

obtaining a polyimide prepolymer having reactive groups originating from a tetracarboxylic component or amino groups at its ends by a reaction between a tetracarboxylic component and a diamine component,

obtaining a polyamic acid prepolymer having amino groups or reactive groups originating from a tetracarboxylic component at its ends by a reaction between a tetracarboxylic component and a diamine component,

a polyamic acid prepolymer having amino groups at its ends being used when the polyimide prepolymer contains reactive groups originating from a tetracarboxylic component at its ends, and

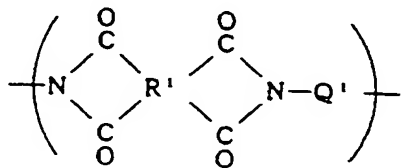
a polyamic acid prepolymer having reactive groups originating from a tetracarboxylic component at its ends being used when the polyimide prepolymer contains amino groups at its ends.

A thin layer forming agent of this invention is featured by:

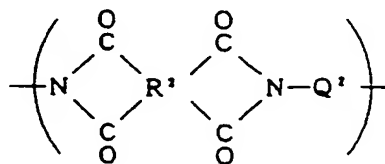
containing a polyimide-type block copolymer having a first polyimide-type block and a second polyimide-type block that is bonded to the first polyimide-type block and has a different structure from the first polyimide-type block;

the first polyimide-type block having recurring units illustrated in formula 1 or 2, and the second polyimide-type block having recurring units illustrated in formula 3 or 4

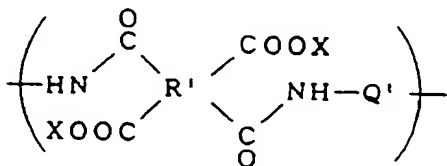
Formula 1



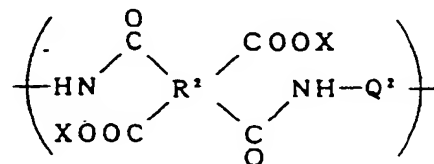
Formula 3



Formula 2



Formula 4



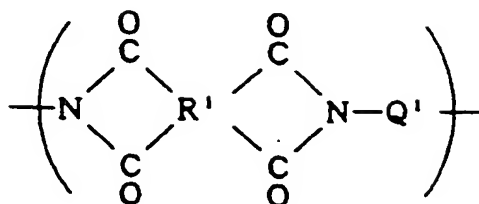
wherein  $\text{R}^1$  and  $\text{R}^2$  are tetravalent organic groups which can be the same or not;  $\text{Q}^1$  and  $\text{Q}^2$  are divalent organic groups which can be the same or not and X is a hydrogen atom or an organic group.)

A liquid crystal alignment layer of this invention is featured by:

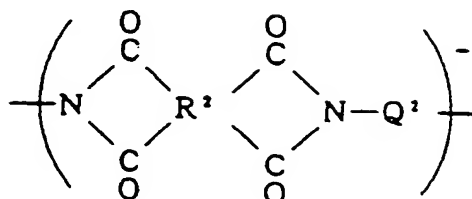
having a polyimide block copolymer comprising, in a molecule, a first polyimide block and a second polyimide block which is bonded to the first polyimide-type block and has a different structure from the first polyimide block,

the first polyimide block having recurring units illustrated in formula 1 and the second polyimide block, having recurring units illustrated in formula 3.

Formula 1



Formula 3



R<sup>1</sup> and R<sup>2</sup> being defined as above.

The present invention further provides a process of producing a liquid crystal alignment layer, comprising a step of producing a thin layer comprising the polyimide block copolymer on a substrate surface and a step of correcting alignment by irradiation on at least a selected region of the thin layer.

The present invention further provides a process of producing a liquid crystal alignment layer, comprising the step of applying a liquid crystal alignment layer forming agent onto a substrate surface to form a thin layer, and a step of aligning the thin layer, the liquid crystal alignment layer forming agent being soluble in organic solvent and being as defined above.

The following will describe details of this invention.

In this specification, the term "component" may refer to a single compound, or a mixture of component of the stated type.

In this specification, the term polyimide-type includes both polyimide and polyamic acid. Therefore, the term polyimide-type block copolymer includes a block copolymer type polyamic acid, a polyimide block copolymer, and a polyimide-polyamic acid block copolymer. The term polyimide-type block includes both a polyamic acid block and a polyimide block.

The term tetracarboxylic component in this specification includes

(1) tetracarboxylic dianhydrides having two divalent carboxylic anhydride groups ( - CO - O - CO - ) bonded to tetravalent nuclear atom group,

(2) tetracarboxylic acids or tetracarboxylic esters having a total of four ( - COOH ) groups and/or ( - COOR ) groups (wherein R is an organic group such as an alkyl group or an aryl group) bonded to tetravalent nuclear atom group, and

(3) tetracarboxylic monoanhydrides or tetracarboxylic ester monohydride having one divalent carboxylic anhydride group and a total of two of ( - COOH ) groups and/or ( - COOR ) groups bonded to tetravalent nuclear atom group.

The polyamic acid prepolymer in this specification is also called an amic acid prepolymer or amic acid oligomer. The polyimide prepolymer is also called an imide oligomer. And the (tetra) carboxylic (di)anhydride in this specification is also called (tetra) carboxylic acid (di) anhydride.

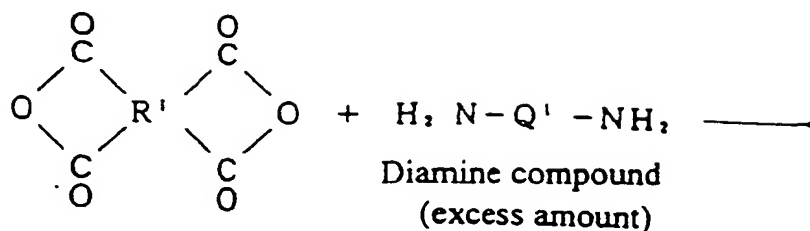
A process of producing a block copolymer type polyamic acid (No. 1): Method A

This process is to produce a block copolymer type polyamic acid comprised of, in a molecule, a first polyamic acid block and a second polyamic acid block having a different structure from the first one. There are three steps in this process.

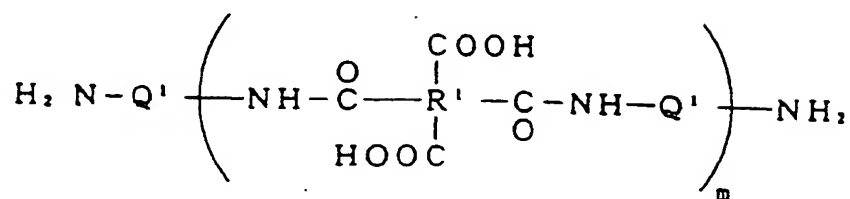
Step 1

Step 1 is the step to produce a first polyamic acid prepolymer having amino groups at molecular ends, by reacting a tetracarboxylic component with a diamine component having two amino groups ( - NH<sub>2</sub>) bonded to a divalent organic group Q<sup>1</sup> illustrated in reaction 1 or 2 below, with the molar ratio of diamine component to tetracarboxylic component of, for example, 1.001 ~ 2.0, in excess of equivalent.

## Reaction 1

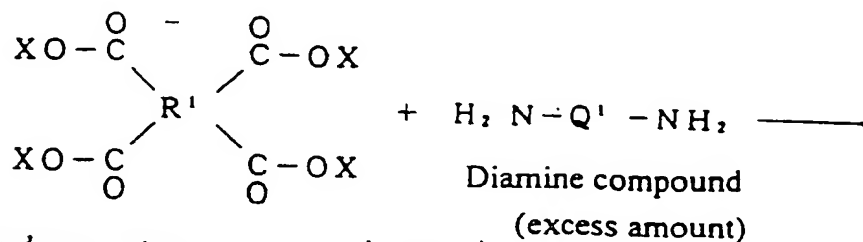


Tetracarboxylic dianhydrides



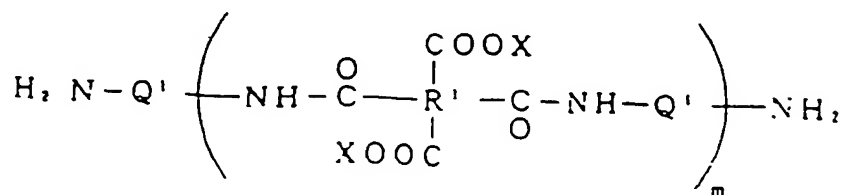
The first polyamic acid prepolymer

## Reaction 2



(X: a hydrogen atom or an organic group)

Tetracarboxylic acid or Tetracarboxylic ester

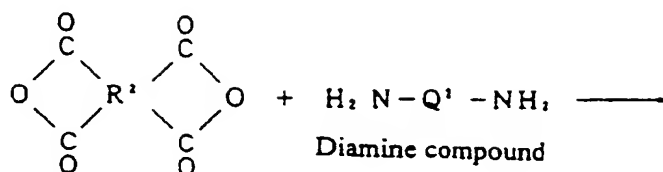


The first polyamic acid prepolymer

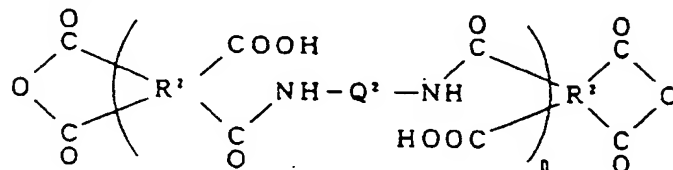
## Step 2

Step 2 is the step to produce a second polyamic acid prepolymer having reactive groups originating from a tetracarboxylic component at molecular ends, by reacting a tetracarboxylic component with a diamine component having two amino groups bonded to a divalent organic group Q<sup>2</sup> as illustrated in reaction 3 or 4 below, with the molar ratio of tetracarboxylic component to diamine component of, for example, 1.001 ~ 2.0, in excess of equivalent.

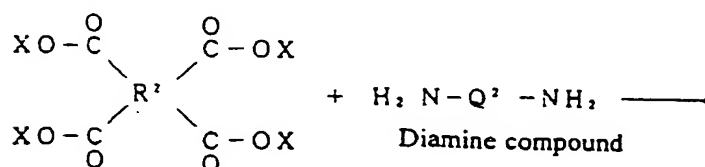
## Reaction 3



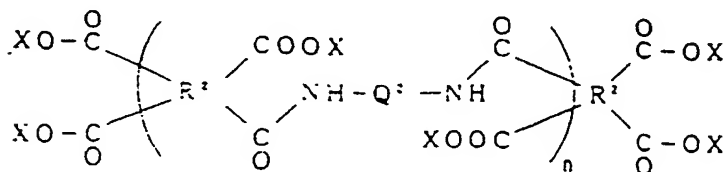
Tetracarboxylic dianhydrides  
(excess amount)



## Reaction 4



(X: a hydrogen atom or an organic group)  
Tetracarboxylic acid or Tetracarboxylic ester  
(excess amount)



## Step 3

Step 3 is the step to produce a block copolymer type polyamic acid by reacting the reaction groups originating from a tetracarboxylic component at the ends of the first polyamic acid prepolymer obtained in Step 1, with the amino groups at the ends of the second polyamic acid prepolymer obtained in Step 2, in the same manner as in Steps 1 or 2; as illustrated in formula 5 below,

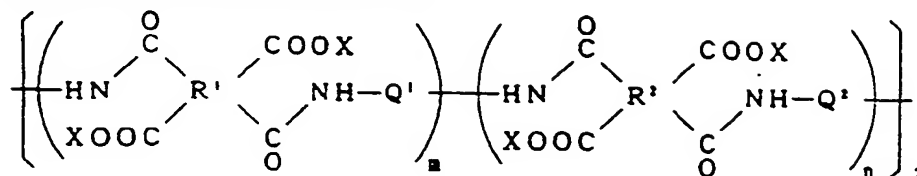
a first polyamic acid block has a recurring bonding unit between a nuclear atom group  $\text{R}^1$  and an organic group  $\text{Q}^1$  via a divalent bonding group ( - CO - NH - ), and

a second polyamic acid block has a recurring bonding unit between a nuclear atom group  $\text{R}^2$  and an organic group  $\text{Q}^2$  via a divalent bonding group ( - CO - NH - ) in the same manner.



## Formula 5

## Block copolymer type polyamic acid



The first polyamic acid block

The second polyamic acid block

(X: a hydrogen atom or an organic group)

As described above, the first and the second polyamic acid prepolymers are structurally different from each other; specifically, molecular structures of recurring units of each polyamic acid prepolymer are different. Referring to Formula 5, nuclear groups  $R^1$  and  $R^2$  can be same or different from each other and organic groups  $Q^1$  and  $Q^2$  can be same or different; however, ( $R^1$  and  $R^2$ ) and ( $Q^1$  and  $Q^2$ ) cannot be same at the same time; at least one set should have different structures.

For this reason, actually, Step 1 and Step 2 may use different component as a tetracarboxylic component, different component as a diamine component, or different component in both cases.

When the tetracarboxylic component and the diamine component used in Step 1 and Step 2 are the same component ( $R^1=R^2$  and  $Q^1=Q^2$  in formula 5), the resulting polymer becomes a homopolymer, not a block copolymer, because the first and the second polyamic acid prepolymers are the same.

Although the amount of either the tetracarboxylic component or the diamine component is used in excess of the other part in Steps 1 and 2, the ratio of component in each step can be selected based on properties required for a final polyimide-type block copolymer. The molar ratio of one to the other is normally in the range of 1.001 ~ 2.0 times.

In Figure 5, the number of recurring Units,  $m$  and  $n$ , in each polyamic acid block is normally in the range of 1 to 1000, preferably 2 to 1000. (This is the same range in reactions 1, 2, 3 and 4, and reactions 5, 6, 7 and 8.) The number of recurring units  $z$  of the bonded body between the first polyamic acid block and the second polyamic acid block is in the range of 1 to 100. When  $z$  is two or more,  $m$  or  $n$  of each recurring unit can be the same, but this is not necessary.

In Method A, it is preferable that the total molar number of tetracarboxylic component in the tetracarboxylic component and that of diamine component in the diamine component used in both Steps 1 and 2 are actually in equivalent relationship.

In each Step 1 and Step 2, plural kinds of component can be used in the tetracarboxylic component and in the diamine component.

By having one kind or more of the polyamic acid prepolymer produced in the same manner as in Step 1 or Step 2, reacted in Step 3 or in the same manner as in Step 3, a block copolymer type polyamic acid comprised of three kinds or more of polyamic acid blocks can be produced.

Above mentioned polyamic acid prepolymer and the block copolymer type polyamic acid may be converted to contain imide bonds in part depending on reaction conditions.

Tetracarboxylic component used in the above Method A are not especially limited. It is preferable, however, that at least one component used in Steps 1 and 2 is a cyclic aliphatic tetracarboxylic compound, from the point of view of solubility of a polyimide block copolymer derived from a block copolymer type polyamic acid in organic solvent.

In view of transparency and liquid crystal alignment properties such as electric properties (when liquid crystal is driving) of a polyimide-block copolymer derived from block copolymer type polyamic acid or the polyamic acid, it is preferable that the diamine component used in Steps 1 and 2 are as follows:

diamine component in one of the steps have two amino groups ( $-NH_2$ ) bonded to an aromatic ring and hetero atoms other than nitrogen atoms of the amino groups;

diamine component in the other step have two amino groups that is bonded to an aromatic ring, and no other hetero atoms than the structural atoms of the amino groups.

#### Tetracarboxylic compounds

Examples of tetracarboxylic dianhydrides include aliphatic tetracarboxylic dianhydrides or cyclic aliphatic tetracarboxylic dianhydrides such as butane tetracarboxylic dianhydride; 1, 2, 3, 4 - cyclobutanetetracarboxylic dianhydride;

- 1, 3 - dimethyl - 1, 2, 3, 4 - cyclobutanetetracarboxylic dianhydride;  
 1, 3 - diethyl - 1, 2, 3, 4 - cyclobutanetetracarboxylic dianhydride;  
 1, 2, 3, 4 - tetramethyl - 1, 2, 3, 4 - cyclobutanetetracarboxylic dianhydride;  
 1, 2, 3, 4 - cyclopentanetetracarboxylic dianhydride;  
 5 2, 3, 5 - tricarboxycyclopentylacetic dianhydride;  
 3, 5, 6 - tricarboxynorbornane - 2 - acetic dianhydride;  
 2, 3, 4, 5 - tetrahydrofuranetetracarboxylic dianhydride;  
 1, 3, 3a, 4, 5, 9b - hexahydro - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) naphtho [1, 2 - c] furan - 1, 3 - dione;  
 1, 3, 3a, 4, 5, 9b - hexahydro - 5 - methyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) naphtho [1, 2 - c] furan - 1, 3 - dione;  
 10 1, 3, 3a, 4, 5, 9b - hexahydro - 5 - ethyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) naphtho [1, 2 - c] furan - 1, 3 - dione;  
 1, 3, 3a, 4, 5, 9b - hexahydro - 7 - methyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) naphtho [1, 2 - c] furan - 1, 3 - dione;  
 1, 3, 3a, 4, 5, 9b - hexahydro - 7 - ethyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) - naphtho [1, 2 - c] furan - 1, 3 - dione;  
 1, 3, 3a, 4, 5, 9b - hexahydro - 8 - methyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) - naphtho [1, 2 - c] furan - 1, 3 - dione;  
 1, 3, 3a, 4, 5, 9b - hexahydro - 8 - ethyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) - naphtho [1, 2 - c] furan - 1, 3 - dione;  
 15 5 - (2, 5 - dioxotetrahydrofural) - 3 - methyl - 3 - cyclohexene - 1, 2 - dicarboxylic dianhydride; bicyclo [2. 2. 2] octo - 7 - en - 2, 3, 5, 6 - tetracarboxylic dianhydride;  
 aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride;  
 3, 3, 4, 4 - benzophenonetetracarboxylic dianhydride;  
 3, 3, 4, 4 - biphenylsulfonetetracarboxylic dianhydride;  
 20 1, 4, 5, 8 - naphthalenetetracarboxylic dianhydride;  
 2, 3, 6, 7 - naphthalenetetracarboxylic dianhydride;  
 3, 3, 4, 4 - biphenylethertetracarboxylic dianhydride;  
 3, 3, 4, 4 - dimethyldiphenylsilanetetracarboxylic dianhydride;  
 3, 3, 4, 4 - tetraphenylsilanetetracarboxylic dianhydride;  
 25 1, 2, 3, 4 - furantetracarboxylic dianhydride;  
 4, 4 - bis (3, 4 - dicarboxyphenoxy) diphenylsulfide dianhydride;  
 4, 4 - bis (3, 4 - dicarboxyphenoxy) diphenylsulfone dianhydride;  
 4, 4 - bis (3, 4 - dicarboxyphenoxy) diphenylpropane dianhydride;  
 3, 3, 4, 4 - perfluoroisopropylidene diphthalic acid dianhydride;  
 30 3, 3, 4, 4 - biphenyltetracarboxylic dianhydride;  
 bis (phthalic acid) - phenylphosphineoxide dianhydride;  
 p - phenylene - bis (triphenylphthalic acid) dianhydride;  
 m - phenylene - bis (triphenylphthalic acid) dianhydride;  
 bis (triphenylphthalic acid) - 4, 4 - diphenylether dianhydride;  
 35 bis (triphenylphthalic acid) - 4, 4 - diphenylmethane dianhydride.

Examples of tetracarboxylic acids include aliphatic tetracarboxylic acids or cyclic aliphatic tetracarboxylic acids such as butanetetracarboxylic acid;

- 1, 2, 3, 4 - cyclobutanetetracarboxylic acid;  
 1, 3 - dimethyl - 1, 2, 3, 4 - cyclobutanetetracarboxylic acid;  
 40 1, 3 - diethyl - 1, 2, 3, 4 - cyclobutanetetracarboxylic acid;  
 1, 2, 3, 4 - tetramethyl - 1, 2, 3, 4 - cyclobutanetetracarboxylic acid;  
 1, 2, 3, 4 - cyclopentane tetracarboxylic acid;  
 2, 3, 5 - tricarboxycyclopentylacetic acid;  
 3, 5, 6 - tricarboxynorbornane - 2 - acetic acid;  
 45 2, 3, 4, 5 - tetrahydrofuranetetracarboxylic acid;  
 5 - (2, 5 - dioxotetrahydrofural) - 3 - methyl - 3 - cyclohexene - 1, 2 - dicarboxylic acid;  
 bicyclo [2. 2. 2] octo - 7 - en - 2, 3, 5, 6 - tetracarboxylic acid;  
 aromatic tetracarboxylic acid such as pyromellitic acid;  
 3, 3, 4, 4 - benzophenonetetracarboxylic acid;  
 50 3, 3, 4, 4 - biphenylsulfonetetracarboxylic acid;  
 3, 3, 4, 4 - biphenylethertetracarboxylic acid;  
 3, 3, 4, 4 - dimethyldiphenylsilanetetracarboxylic acid;  
 1, 2, 3, 4 - furantetracarboxylic acid;  
 4, 4 - bis (3, 4 - dicarboxyphenoxy) diphenylsulfide;  
 55 4, 4 - bis (3, 4 - dicarboxyphenoxy) diphenylsulfone;  
 3, 3, 4, 4 - perfluoroisopropylidenediphthalic acid;  
 3, 3, 4, 4 - biphenyltetracarboxylic acid;  
 p - phenylene - bis (triphenylphthalic acid);

m - phenylene - bis (triphenylphthalic acid);  
bis (triphenylphthalic acid) - 4, 4 - diphenylmethane.

Examples of tetracarboxylic esters include methyl ester, ethyl ester, propyl ester, isopropyl ester and butyl ester of above mentioned carboxylic acids. Specifically, examples are pyromellitic acid tetramethyl ester, pyromellitic acid tetra-

ethyl ester, pyromellitic acid tetrapropyl ester, pyromellitic acid tetraisopropyl ester and pyromellitic acid tetrabutyl ester.

Among them, tetracarboxylic anhydrides are preferable. Especially, cyclic aliphatic tetracarboxylic dianhydrides

such as

2, 3, 5 - tricarboxycyclopentylacetic dianhydride;

1, 2, 3, 4 - cyclobutanetetracarboxylic dianhydride;

1, 3 - dimethyl - 1, 2, 3, 4 - cyclobutanetetracarboxylic dianhydride;

1, 3, 3a, 4, 5, 9b - hexahydro - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) - naphtho [1, 2 - c] - furan - 1, 3 - dione;

1, 3, 3a, 4, 5, 9b - hexahydro - 5 - methyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) - naphtho [1, 2 - c] - furan - 1, 3 - dione;

1, 3, 3a, 4, 5, 9b - hexahydro - 5 - ethyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) - naphtho [1, 2 - c] - furan - 1, 3 - dione;

1, 3, 3a, 4, 5, 9b - hexahydro - 7 - methyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) - naphtho [1, 2 - c] - furan - 1, 3 - dione;

1, 3, 3a, 4, 5, 9b - hexahydro - 7 - ethyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) - naphtho [1, 2 - c] - furan - 1, 3 - dione;

1, 3, 3a, 4, 5, 9b - hexahydro - 8 - methyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) - naphtho [1, 2 - c] - furan - 1, 3 - dione;

1, 3, 3a, 4, 5, 9b - hexahydro - 8 - ethyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) - naphtho [1, 2 - c] - furan - 1, 3 - dione.

Also other preferable tetracarboxylic dianhydrides are butanetetracarboxylic dianhydride; pyromellitic acid dianhydride;

3, 3, 4, 4 - benzophenonetetracarboxylic dianhydride;

3, 3, 4, 4 - biphenylsulfonetetracarboxylic dianhydride;

1, 4, 5, 8 - naphthalenetetracarboxylic dianhydride;

2, 3, 6, 7 - naphthalenetetracarboxylic dianhydride;

3, 3, 4, 4 - biphenylethertetracarboxylic dianhydride.

These tetracarboxylic compounds can be used alone or in a combination of two kinds or more.

#### Diamine Compounds

Examples of diamine compounds include aromatic diamine compounds such as

p - phenylenediamine;

m - phenylenediamine;

4, 4 - diaminodiphenylmethane;

4, 4 - diaminodiphenylethane;

4, 4 - diaminodiphenylsulfide;

4, 4 - diaminodiphenylsulfone;

3, 5 - diamino - 3 - trifluoromethylbenzanilide;

3, 5 - diamino - 4 - trifluoromethylbenzanilide;

3, 3 - dimethyl - 4, 4 - diaminobiphenyl;

4, 4 - diaminobenzanilide;

4, 4 - diaminodiphenyl ether;

1, 5 - diaminonaphthalene;

5 - amino - 1 - (4 - aminophenyl) - 1, 3, 3 - trimethylindan;

6 - amino - 1 - (4 - aminophenyl) - 1, 3, 3 - trimethylindan;

3, 4 - diaminodiphenyl ether;

3, 3 - diaminobenzophenone;

3, 4 - diaminobenzophenone;

4, 4 - diaminobenzophenone;

2, 2 - bis [4 - (4 - aminophenoxy) phenyl] propane;

2, 2 - bis [4 - (4 - aminophenoxy) phenyl] hexafluoropropane;

2, 2 - bis (4 - aminophenyl) hexafluoropropane;

bis [4 - (4 - aminophenoxy) phenyl] sulfone;

1, 4 - bis (4 - aminophenoxy) benzene;

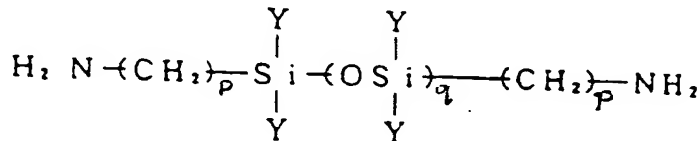
1, 3 - bis (4 - aminophenoxy) benzene;

1, 3 - bis (3 - aminophenoxy) benzene;

9, 9 - bis (4 - aminophenyl) - 10 - hydroanthracene;

2, 7 - diaminofluorene;

9, 9 - bis (4 - aminophenyl) fluorene;  
 4, 4 - methylene - bis (2 - chloroaniline);  
 2, 2, 5, 5 - tetrachloro - 4, 4 - diaminobiphenyl;  
 2, 2 - dichloro - 4, 4 - diamino - 5, 5 - dimethoxybiphenyl;  
 3, 3 - dimethoxy - 4, 4 - dimethoxybiphenyl;  
 4, 4 - (p - phenyleneisopropylidene) bisaniline;  
 4, 4 - (m - phenyleneisopropylidene) bisaniline;  
 2, 2 - bis [4 - (4 - amino - 2 - trifluoromethylphenoxy) phenyl] hexafluoropropane;  
 4, 4 - diamino - 2, 2 - bis (trifluoromethyl) biphenyl;  
 4, 4 - bis [(4 - amino - 2 - trifluoromethyl) phenoxy] - octafluorobiphenyl;  
 bis (4 - aminophenoxy) - 2, 2 - dimethylpropane;  
 aromatic diamine compounds having hetero atoms such as diaminotetraphenylthiophene; aliphatic or cyclic  
 aliphatic diamine compounds such as  
 1, 1 - metaxylilene diamine;  
 1, 3 - propane diamine;  
 tetramethylene diamine;  
 pentamethylene diamine;  
 hexamethylene diamine;  
 heptamethylene diamine;  
 octamethylene diamine;  
 nonamethylene diamine;  
 1, 7 - diaminooctamethylene diamine;  
 1, 4 - diaminocyclohexane;  
 isophorone diamine;  
 tetrahydrodicyclopentadienylene diamine;  
 hexahydro - 4, 7 - methanoindanilenedimethylene diamine;  
 tricyclo [6. 2. 1. 02, 7] - undecylenedimethyl diamine;  
 4, 4 - methylene bis (cyclohexylamine);  
 diamino organosiloxane according to the following Formula.



[wherein Y is a hydrocarbon group having 1 to 12 carbon atoms such as an alkyl group, for example, a methyl  
 group, an ethyl group or a propyl group; a cycloalkyl group, for example, a cyclohexyl group; an aryl group, for example,  
 a phenyl group; p is an integer from 1 to 3 and q is an integer from 1 to 20.]

Among them, preferable compounds are

p - phenylenediamine;  
 4, 4 - diaminodiphenylmethane;  
 1, 5 - diaminonaphthalene;  
 2, 7 - diaminofluorene;  
 4, 4 - diaminodiphenyl ether;  
 4, 4 - (p - phenyleneisopropylidene) bisaniline;  
 2, 2 - bis [4 - (4 - aminophenoxy) phenyl] hexafluoropropane;  
 2, 2 - bis (4 - aminophenyl) hexafluoropropane;  
 2, 2 - bis [4 - (4 - amino - 2 - trifluoromethylphenoxy) phenyl] hexafluoropropane;  
 4 - 4 - diamino - 2, 2 - bis (trifluoromethyl) biphenyl;  
 4 - 4 - bis [(4 - amino - 2 - trifluoromethyl) phenoxy] - octafluorobiphenyl; and  
 3, 5 - diamino - 4 - trifluoromethylbenzanilide.

Especially preferable are p - phenylenediamine, 4 - 4 - diaminodiphenyl methane, and 4 - 4 - (p - phenyleneisopro-  
 pylidene) bisaniline. These diamine compounds can be used as alone or a combination of two kinds or more.

Examples of above mentioned aromatic diamine compounds, that have two amino groups ( - NH<sub>2</sub>) bonded to the  
 aromatic ring and have hetero atoms such as oxygen atoms and sulfur atoms other than the nitrogen atoms of the  
 amino groups, include the compounds A01 through A14 illustrated in Claim 16.

The polycondensation reaction between the tetracarboxylic component and the diamine component in Steps 1 or 2 takes place normally in the range of 0 to 200°C, preferably 0 to 100°C.

Any organic solvents that dissolve the resulting polyamic acid can be used in this polycondensation reaction. Examples include non-proton type polar solvents such as N - methyl - 2 - pyrrolidone; N, N - dimethylacetamide; N, N - dimethylformamide; dimethylsulfoxide; (γ butyrolactone; tetramethyl urea; and hexamethyl phosphortriamide; phenol type solvents such as m-cresol, xylene, phenol, and phenol halide. Regarding the amount of the organic solvent used, the total amount of tetracarboxylic compounds and diamine compounds should be preferably in the range of 0.1 to 30 weight % of the total amount of reaction solution.

With these organic solvents, poor solvents such as alcohols, ketones, esters, ethers, hydrocarbon halides and hydrocarbons can be used within a proportion such that the resulting polyamic acid prepolymer does not precipitate. Examples of the poor solvents include methyl alcohol, ethyl alcohol, isopropyl alcohol, cyclohexanol, ethylene glycol, propylene glycol, 1, 4 - butanediol, triethylene glycol, acetone, methylethylketone, methylisobutylketone, cyclohexanone, methyl acetate, ethyl acetate, butyl acetate, diethyl oxalate, diethyl malonate, diethyl ether, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol n-propyl ether, ethylene glycol isopropyl ether, ethylene glycol n-butyl ether, ethylene glycol dimethyl ether, ethylene glycol ethyl ether acetate, diethylene glycol dimethyl ether, tetrahydrofuran, dichloromethane, 1, 2 - dichloroethane, 1, 4 - dichlorobutane, trichloroethane, chlorobenzene, o-dichlorobenzene, hexane, heptane, octane, benzene, toluene, and xylene.

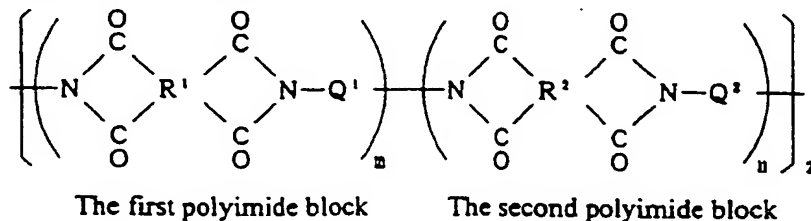
#### A process of producing a polyimide block copolymer from the mentioned polyamic acid:

##### Method B

The block copolymer type polyamic acid obtained by Method A can be imidized and its ring can be closed by dehydration reaction to produce block copolymer type polyamic acid comprising a first polyimide block with a recurring unit of a bonding between a nuclear atom group R<sup>1</sup> and an organic group Q<sup>1</sup> via an imide bond, and a second polyimide block with a recurring unit of a bonding between a nuclear group R<sup>2</sup> and an organic group Q<sup>2</sup> in the same manner.

#### Formula 6

##### Polyimide block copolymer



To be more specific, imidization is implemented to dehydrate and close the ring of polyamic acid by heating the mentioned polyamic acid or dissolving the mentioned polyamic acid into an organic solvent and heating the solution in the presence of a dehydrating agent and an imidization catalyst.

Heat imidization is implemented normally at 60 to 250°C, preferably at 100 to 200°C. At less than 60°C, the ring closing dehydration reaction does not progress efficiently; at more than 200°C, the resulting polyimide block copolymer may have a small molecular weight.

When imidization is implemented by adding a dehydrating agent and imidization catalyst into a solution of block copolymer type polyamic acid, the dehydrating agent can be selected from acid anhydrides such as acetic anhydride, propionic anhydride, trifluoro acetic anhydride. The amount of the dehydrating agent per mole of recurring units of the polyamic acid is preferably 1.6 to 20 mole.

Examples of the imidization catalyst include tertiary amines such as pyridine, collidine, lutidine, triethylamine, but are not limited. The amount of the imidization catalyst per mole of the dehydrating agent is preferably 0.5 to 10 mole. Organic solvents used in imidization include those organic solvents mentioned as examples for synthesis of block copolymer type polyamic acid; the reaction temperature for the ring closing dehydration reaction during imidization is normally 0 to 200°C, preferably 60 to 150°C.

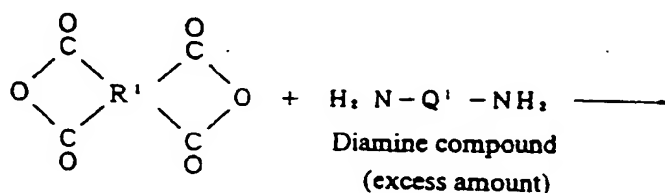
A process of directly producing a polyimide block copolymer (No. 1): Method C

This method directly produces a polyimide block copolymer comprising, in a molecule, a first polyimide-type block and a second polyimide block with a different structure from the first polyimide block as illustrated in formula 6 above, by the reaction between a tetracarboxylic component and a diamine component in the same manner as in the process of producing block copolymer type polyamic acid. There are three steps in this method:

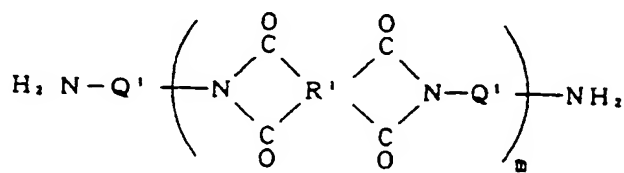
## Step 1

Step 1 is the step to produce a first polyimide prepolymer having amino groups at molecular ends, by the reaction between a tetracarboxylic component and a diamine component having two amino groups bonded to a divalent organic group  $Q^1$ , as illustrated in reaction 5 or 6 below, with the molar ratio of diamine compounds to tetracarboxylic compounds of, for example, 1.001 to 2.0 in excess of equivalent.

## Reaction 5

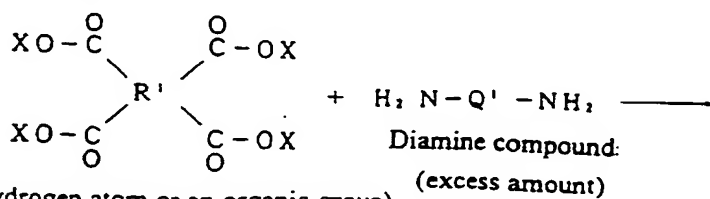


Tetracarboxylic dianhydrides



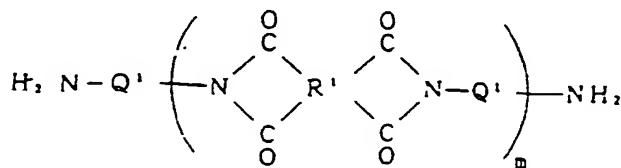
The first polyimide prepolymer

## Reaction 6



(X: a hydrogen atom or an organic group)

Tetracarboxylic acid or Tetracarboxylic ester

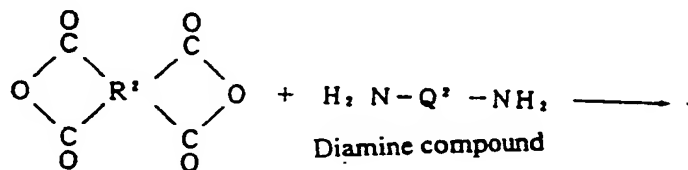


The first polyimide prepolymer

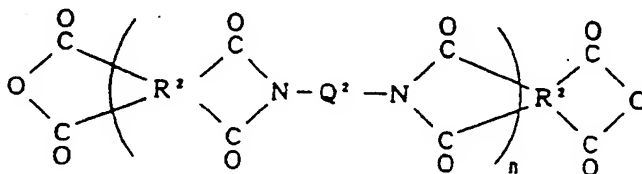
## Step 2

Step 2 is a step to produce a second polyimide prepolymer having reactive groups originating from a tetracarboxylic component at molecular ends, by the reaction between a tetracarboxylic component and a diamine component having two amino groups bonded to a divalent organic group  $Q^2$  as illustrated in reaction 7 or 8 below, with the molar ratio of tetracarboxylic compounds to diamine compounds of, for example, 1.001 to 2.0 in excess of equivalent.

## Reaction 7

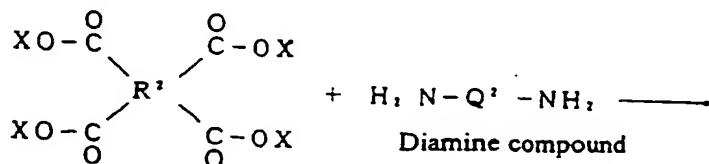


Tetracarboxylic dianhydrides  
(excess amount)



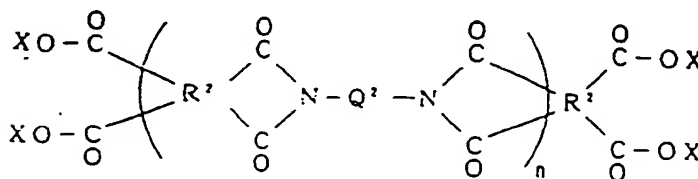
The second polyimide prepolymer

## Reaction 8



(X: a hydrogen atom or an organic group)

Tetracarboxylic acid or Tetracarboxylic ester  
(excess amount)



The second polyimide prepolymer

To produce polyimide prepolymers in the above Steps, a dehydrating agent and an imidization catalyst required for imidization need to be added to the reaction system in presence of the same organic solvent as in Method A and to be heated at an appropriate temperature, for example, 0 to 200°C, preferably 60 to 150°C, for a reaction.

The first and second polyimide prepolymers may be produced by producing a first and a second polyamic acid prepolymers according to Steps 1 and 2 in Method A, and then, imidizing them respectively as in Method B.

## Step 3

Step 3 is a step to produce a polyimide block copolymer by reaction between the amino groups at the ends of the first polyimide prepolymer obtained in Step 1 and the reaction groups originating from the tetracarboxylic component at the ends of the second polyimide prepolymer obtained in Step 2;

a first polyimide block has a recurring bonding unit between a nuclear group  $R^1$  and an organic group  $Q^1$ , and a second polyimide-type block has recurring bonding unit between a nuclear group  $R^2$  and an organic group  $Q^2$  as illustrated in formula 6 above.

The various conditions of the polyimide block copolymer are the same as in those of polyimide block copolymer obtained from the block copolymer type polyamic acid: in each of Steps 1 and 2, the ring closing dehydration reaction occurs by the imidization, thus eliminating Steps in Method B to produce polyimide block copolymer. This process is different from that in Method A only in this sense. The condition details of this Method C, therefore, remain the same as in Method A and Method B.

In Steps 1 or 2, plural kinds of compounds can be used in the tetracarboxylic component and plural kinds of compounds can be used in the diamine components. By having one or more kinds of polyimide prepolymer produced in the same manner as in Step 1 or 2 reacted in Step 3 or in the same manner as in the Step 3, polyimide block copolymer comprised of three or more kinds of polyimide block can be produced.

A process of directly producing polyimide block copolymer (No. 2): Method D

This method employs a diisocyanate component in place of a diamine component in the Method C. Except that the amino groups of reaction 5 of the Figure 11 and reaction 7 of the Figure 12 are replaced with isocyanate groups, the details remain the same as in Method C: polyimide-type block copolymer is produced in the same manner of Steps 1 through 3 of Method C.

Examples of diisocyanate compounds include aliphatic diisocyanate compounds such as hexamethylene diisocyanate; cyclic aliphatic diisocyanate compounds such as cyclohexane diisocyanate; and aromatic diisocyanate compounds such as

diphenylmethane - 4, 4 - diisocyanate;

diphenyl ether - 4, 4 - diisocyanate;

diphenylsulfone - 4, 4 - diisocyanate;

diphenylsulfide - 4, 4 - diisocyanate;

1, 2 - diphenylethane - p, p - diisocyanate;

2, 2 - diphenylpropane - p, p - diisocyanate;

2, 2 - diphenyl - 1, 1, 1, 3, 3, 3 - hexafluoropropane - p, p - diisocyanate;

2, 2 - diphenylbutane - p, p - diisocyanate;

diphenyldichloromethane - 4, 4 - diisocyanate;

diphenylfluoromethane - 4, 4 - diisocyanate;

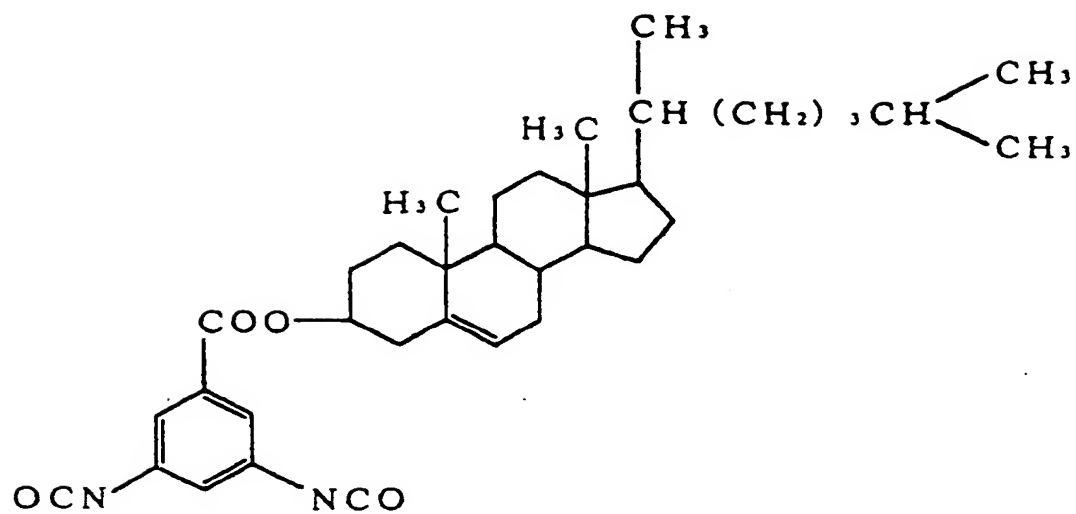
benzophenone - 4, 4 - diisocyanate;

N - phenylbenzoic amide - 4, 4 - diisocyanate.

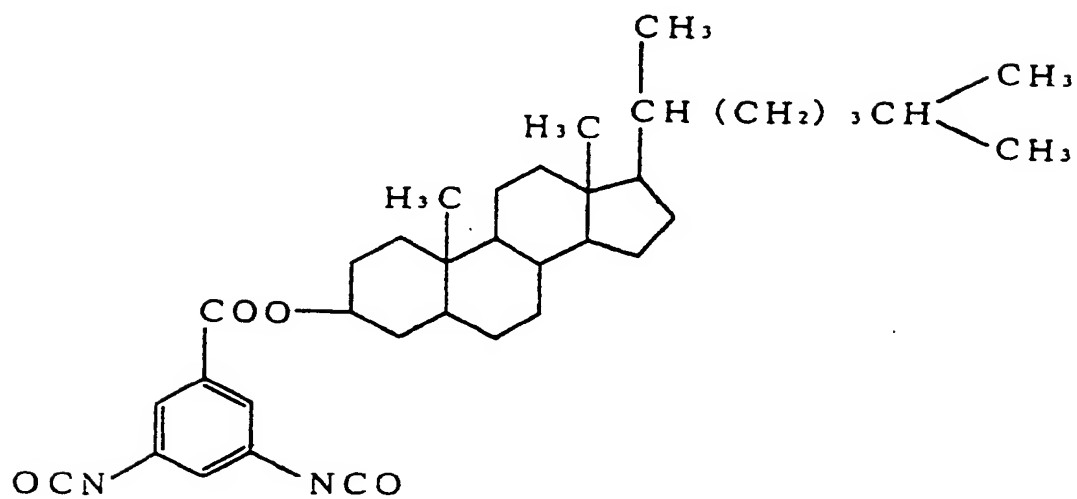
Examples of aromatic diisocyanate compounds having two isocyanate groups (NCO) bonded to the aromatic ring and having heteroatoms other than nitrogen atoms of the isocyanate groups, are illustrated as compounds B01 through B14 in the following formulae



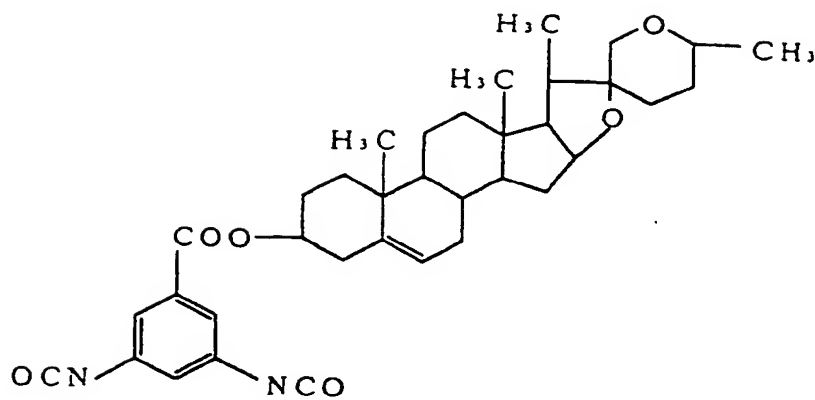
B01



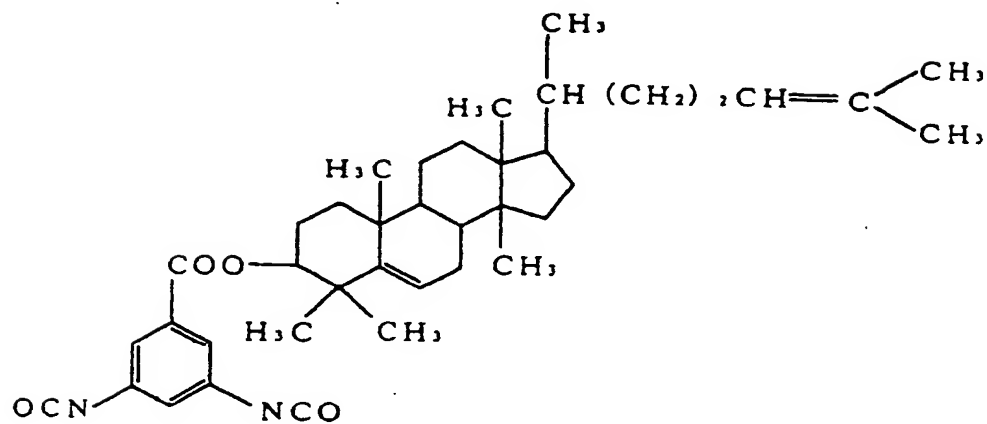
B02



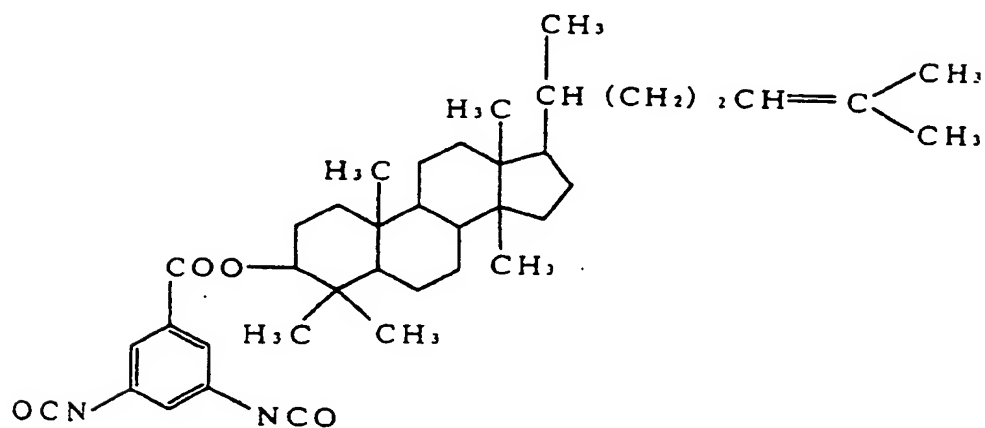
B03



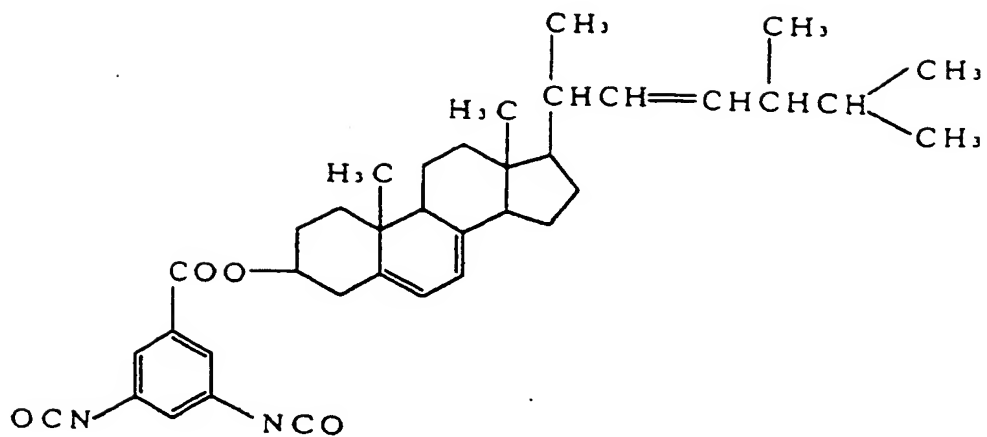
B04



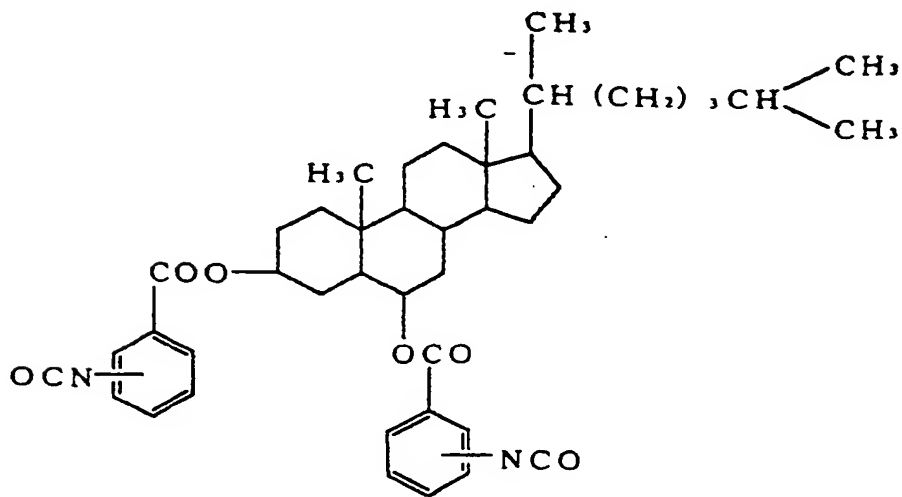
B05



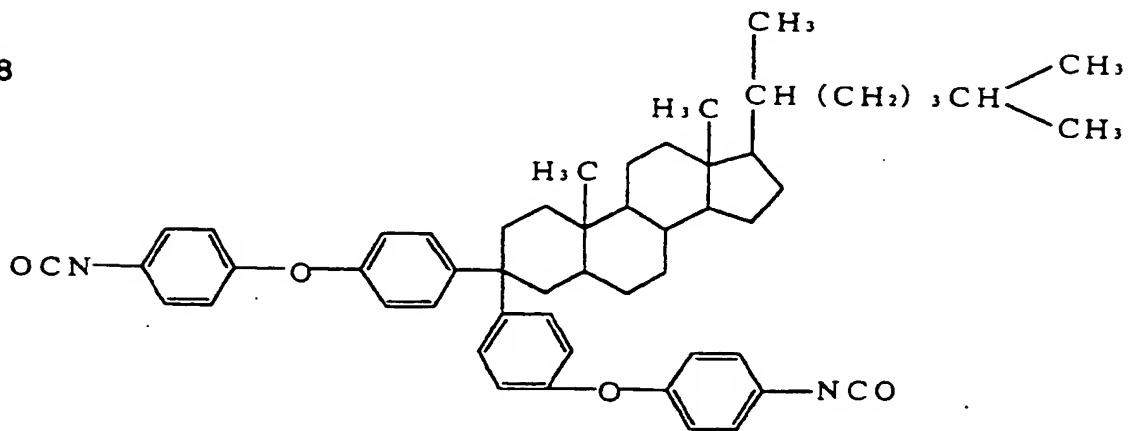
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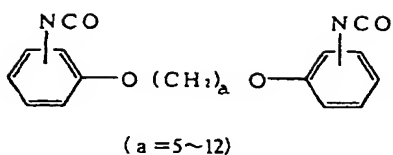
**B07**



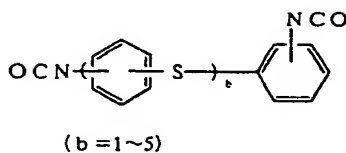
808



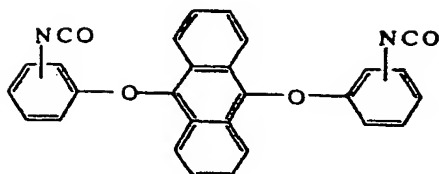
B09



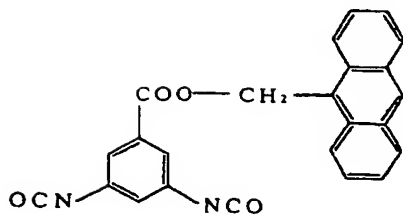
B10



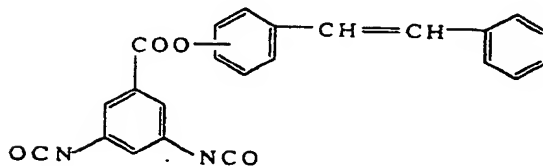
B11



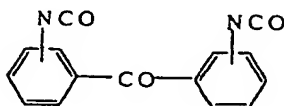
B12



B13



B14



These isocyanate components can comprise a single compound or a combination of two or more compounds.

One of the diisocyanate compounds used in Steps 1 and 2 is preferably an aromatic diisocyanate compound having two isocyanate groups (NCO) bonded to an aromatic ring and having heteroatoms other than the nitrogen atoms of the isocyanate group, while the other diisocyanate compound is preferably an aromatic diisocyanate compound having two

isocyanate groups bonded to an aromatic ring and not having heteroatoms other than the nitrogen atoms of the isocyanate group, because of the transparency of the polyimide block copolymer and because of the liquid crystal alignment properties, such as electric properties during liquid crystal driving.

For the reaction between tetracarboxylic compounds and diisocyanate compounds, catalysts are not specially required, but the reaction temperature is normally between 50 and 200°C, preferably between 100 and 160°C.

In Step 1 or Step 2, plural kinds of compounds can be used in the tetracarboxylic component and plural kinds of compounds can also be used in the diisocyanate component. By having one or more kinds of polyimide prepolymer produced in the same manner as in Step 1 or Step 2 reacted in Step 3, or in the same manner as in the Step 3, polyimide block copolymer comprised of three or more kinds of polyimide blocks can be produced.

#### A process of producing a polyimide-polyamic acid block copolymer (No. 1):

##### Method E

This method is comprised of the following steps:

a step to obtain a polyimide prepolymer having carboxylic anhydride groups or isocyanate groups at its ends in the same manner as mentioned in mentioned Method D, using a tetracarboxylic dianhydride component and a diisocyanate component; a step to obtain a polyamic acid prepolymer having amino groups or carboxylic anhydrides groups at its ends in the same manner as in mentioned Method A, using a tetracarboxylic dianhydride component and a diamine component;

and a step to obtain a polyimide-polyamic acid block copolymer by having the polyimide prepolymer reacted with the polyamic acid prepolymer after selecting functional groups at their ends.

The details of the steps are the same as mentioned Method D or Method A.

#### A process of producing a polyimide - polyamic acid block copolymer (No. 2):

##### Method F

This method is comprised of the following steps:

a step to obtain a polyimide prepolymer having reactive groups originating from a tetracarboxylic component or amino groups at its ends in the same manner as in Method C, using a tetracarboxylic component and a diamine component; a step to obtain a polyamic acid prepolymer having amino groups or reactive groups originating from a tetracarboxylic component at its ends in the same manner as in Method A by using a tetracarboxylic component and a diamine component;

and a step to obtain a polyimide-polyamic acid block copolymer by having the polyimide prepolymer reacted with the polyamic acid prepolymer after selecting functional groups at their ends.

The details of the process are the same as described in Method C or Method A.

As described above, Method A of this invention can produce a block copolymer type polyamic acid having recurring units of the first polyamic acid prepolymer block and the second polyamic acid prepolymer block with different structure from the first polyamic acid prepolymer block.

Then, by imidizing the block copolymer type polyamic acid obtained in Method A, according to Method B of this invention, a polyimide block copolymer can be produced.

According to Method C or D of this invention, a polyimide block copolymer can be produced directly.

According to Method E or F, of this invention a polyimide - polyamic acid block copolymer can be produced.

This polyimide-block copolymer is comprised of two, three, or more kinds of polyimide block components of different structures. As a result, it basically has inherent properties of a polyamic acid or a polyimide and, at the same time, has plural kinds of homopolymer properties of polyamic acid or polyimide related to each block component. In other words, coexistence of block components in a molecule, that is the first and the second polyimide components, provides the properties of the homopolymer of the first polyimide block components and the properties of the homopolymer of the second polyimide block components at the same time. It can also be said that the properties of the polyimide block copolymer is the status in which the homopolymer properties of polyimide constituting certain block components are modified by the homopolymer properties of polyimide constituting the other blocks.

Such properties can be obtained neither from a mere mixture of the first polyimide and the second polyimide nor from, for example, a polycondensation reaction of all tetracarboxylic component, diamine compounds or diisocyanates used for the first polyimide and the second polyimide.

That is, the process for producing a polyimide block copolymer of this invention can produce a polyimide block copolymer with excellent plural properties coexistently which are difficult to obtain at the same time by conventional methods.

In both above and below, when organic groups  $R^1$ ,  $R^2$ ,  $Q^1$ , or  $Q^2$  exist in plural in the formulas of polyimide-block copolymer, they have the same structure as each other.

As described above, the properties of a polyimide-type block copolymer depends on the structures of recurring units in each block element of the polyimide-type block copolymer and the number of recurring units or its recurring ratio. Therefore, by controlling these factors, it is possible to control the properties of a polyimide-block copolymer which is finally obtained. Since each polycondensation reaction by the method of this invention is performed in a simple way, the conditions can be controlled very easily.

That is, the properties of a polyimide-type block which is finally obtained can be controlled by selecting the kinds and by adjusting its quantity or ratio used from such compounds as tetracarboxylic compounds, diamine compounds or diisocyanate compounds, so that the number, kind and ratio of the block components that constitute polyimide-type block copolymer, kinds of compounds and the (ratio) quantity can be controlled.

As a result, polyimide-type copolymer having desired properties can be produced by molecular design in accordance with actual applications, based on the empirically known properties of polyimide homopolymer.

Also, the polyimide block copolymer may be of an end-modified type in which a monoanhydride or monoamine compound and the like is bonded to its ends to control its molecular weight. Such an end-modified type can be synthesized by adding a monoanhydride or monoamine compound and the like to the reaction system when polyamic acid or polyimide is synthesized.

Examples of monoanhydrides are maleic anhydride, phthalic acid anhydride, or nadic anhydride; examples of monoamine compounds are aniline, cyclohexylamine, n-butylamine, n-pentylamine, n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine, n-decylamine, n-undecylamine, n-dodecylamine, n-tridecylamine, n-tetradecylamine, n-pentadecylamine, n-hexadecylamine, n-heptadecylamine, n-octadecylamine, n-eicosylamine.

The polyimide block copolymer can be of the end-modified type obtained by adding a polyamic acid compound or an imide compound, having a monoanhydride or monoamine compound at its end to the reaction system.

#### A thin layer forming agent

A thin layer forming agent of this invention is a liquid body obtained by dissolving the block copolymer type polyamic acid, polyimide block copolymer, or polyimide-polyamic acid block copolymer into appropriate organic solvent as a major component.

By being comprised of polyimide-type block copolymer, this thin layer forming agent can be used to form a thin layer for various purposes, for example, an electrical insulator, a heat-resistant coating, a surface protection coating, and others. The agent is especially useful as a liquid crystal alignment layer forming agent.

The organic solvent for a thin layer forming agent is not limited and various kinds can be used if it dissolves the block copolymer type polyamic acid, the polyimide block copolymer, or the polyimide-polyamic acid block copolymer.

Examples are mentioned as reaction solvents used in above Method A.

To a thin layer forming agent, various additives can be added in accordance with its usage. Especially, a thin layer forming agent used as a liquid crystal alignment layer forming agent may contain various additives to improve properties of its own and that of the liquid crystal alignment layer formed from it.

Such additives can contain functional silane-containing compounds, for example, to improve the adhesiveness of the liquid crystal alignment layer to a substrate surface of a liquid crystal display element. Examples of functional silane-containing compounds are:

3 - aminopropyltrimethoxysilane; 3 - aminopropyltriethoxysilane;

2 - aminopropyltrimethoxysilane; 2 - aminopropyltriethoxysilane;

N - (2-aminoethyl) - 3 - aminopropyltrimethoxysilane;

N - (2 - aminoethyl) - 3 - aminopropylmethyldimethoxysilane;

3 - ureidopropyltrimethoxysilane; 3 - ureidopropyltriethoxysilane;

N - ethoxycarbonyl - 3 - aminopropyltrimethoxysilane;

N - ethoxycarbonyl - 3 - aminopropyltriethoxysilane;

N - triethoxysilylpropyltriethylenetriamine;

N - trimethoxysilylpropyltriethylenetriamine;

10 - trimethoxysilyl - 1, 4, 7 - triazadecane;

10 - triethoxysilyl - 1, 4, 7 - triazadecane;

9 - trimethoxysilyl-3, 6 - diazanonyl acetate;

9 - triethoxysilyl - 3, 6 - diazanonyl acetate;

N - benzyl - 3 - aminopropyltrimethoxysilane;

N - benzyl - 3 - aminopropyltriethoxysilane;

N - phenyl - 3 - aminopropyltrimethoxysilane;

N - phenyl - 3 - aminopropyltriethoxysilane;

N - bis (oxyethylene) - 3 - aminopropyltrimethoxysilane; and  
 N - bis (oxyethylene) - 3 - aminopropyltriethoxysilane.

### Thin Layer Formation

In order to form a thin layer using the thin layer forming agent, the thin layer forming agent is normally applied on the surface of a proper substrate and dried, and further heated, if necessary, for ring closing dehydration reaction when there are polyamic acid blocks. When using this layer forming agent as a liquid crystal alignment layer forming agent, a liquid crystal alignment layer is formed and a liquid crystal display element is produced by, for example, the following process:

(1) The thin layer forming agent is applied on a surface of a liquid crystal display element substrate, on which a transparent conductive layer is prepared, and the applied surface of the substrate is heated to form a thin layer.

Examples of substrates include glasses such as float glass and soda glass; a transparent substrate comprised of plastics such as polyethyleneterephthalate, polybutylene terephthalate, polyether sulfone, and polycarbonate.

Examples of transparent conductive layers formed on a substrate are NESA layer (U.S. PPG registered trademark) comprised of tin oxide ( $\text{SnO}_2$ ), ITO layer comprised of indium oxide - tin oxide ( $\text{In}_2\text{O}_3 - \text{SnO}_2$ ), and the like. As Examples of the patterning method of these transparent conductive layers, a photo-etching method, a method preliminary using a mask and the like can be used. Other applications of the thin layer forming agent include a printing method, a roll-coater method, a spinner method, and a curtain coat method and the like.

Regarding the application of a thin layer forming agent, a functional silane compound, a functional titanium compound, and the like may be preliminarily applied on a substrate and on a transparent conductive layer to improve the adhesiveness of the applied layer to the substrate surface and the transparent conductive layer. The temperature during heating of the applied surface or ring closing dehydration reaction of polyamic acid block is in the range of 80 to 200°C, preferably 120 to 200°C. A dried layer thickness of the applied layer to be formed is usually in the range of 0.001 to 1  $\mu\text{m}$ , preferably 0.005 to 0.5  $\mu\text{m}$ .

(2) The obtained thin layer is aligned. Examples of the alignment treatment of thin layers are methods of rubbing, irradiating with ultraviolet light, and the like. A method of rubbing is to rub a thin layer in a certain direction with a roll wound with, for example, nylon, rayon, cotton cloths, and the like. By the alignment treatment, the thin layer molecules are given alignability of liquid crystal molecules to form a liquid crystal alignment layer.

Before or after an aligning treatment, one may perform correcting alignment treatment by irradiating, for example, with ultraviolet light in the range of 1 to 10000  $\text{mJ}/\text{cm}^2$ , preferably 200 to 3000  $\text{mJ}/\text{cm}^2$  on the selected partial area of the formed thin layer.

(3) Two substrates on which liquid crystal alignment layers were formed in above manner are prepared. The substrates are put together so that the rubbing directions of the liquid crystal alignment layers are orthogonal, parallel or reversed parallel to the rubbing direction of the opposite side via a cell gap. The peripherals are sealed with a sealing agent. Liquid crystals are injected into the cell gap that is spaced between the substrate surfaces and sealing agent. Then, the inlet is sealed to constitute a liquid crystal cell. Polarizers are attached, in accordance with or orthogonal to the rubbing direction of the liquid crystal alignment layer. Polarizers are attached on one substrate on the outer surfaces of a liquid crystal cell, that is, on the other surface side of each substrate that constitutes the liquid crystal cell, to obtain the liquid crystal display element.

Examples of the sealing agents include epoxy resin containing a curing agent and aluminum oxide particles as a spacer and the like.

Examples of liquid crystal materials include nematic type liquid crystals and smectic type liquid crystals. Of these, nematic type liquid crystals are preferable. Examples of nematic type liquid crystals are Schiffs base type liquid crystal, azoxy type liquid crystal, biphenyl liquid type crystal, phenylcyclohexane type liquid crystal, ester type liquid crystal, terphenyl type liquid crystal, biphenylcyclohexane type liquid crystal, pyrimidine type liquid crystal, dioxane type liquid crystal, bicyclooctane type liquid crystal and cubane type liquid crystal and the like. Further, ferroelectric type liquid crystals such as p-decyloxybenzylidene-p-amino-2-methylbutyl cinnamate can be used.

Cholesteric type liquid crystals such as cholesteryl chloride, cholesteryl nonaate, and cholesteryl carbonate or chiral agents, for example, with product names C-15, CB-15 (Merck Product) can be added to these liquid crystals.

Examples of polarizers attached on the outer surface of liquid crystal cell include a polarizer of which the polarizing layer is comprised of a so-called H-layer, in which iodine is absorbed while polyvinyl alcohol is stretch-aligned and is sandwiched between acetyl cellulose protective layers, or the polarizer of which the polarizing layer consists of H-layer only and the like.

A liquid crystal alignment layer of this invention is basically comprised of polyimide block copolymer having the composition of formula 6 above. As described above, the polyimide block copolymer provides excellent plural properties together which is difficult to obtain at the same time by conventional methods.

For example, it will be apparent from the examples described later that a certain kind of polyimide made by conventional methods provides excellent applicability, but the alignment properties of its liquid crystal alignment layer are not stable being dependent on the rubbing times or layer thickness; on the other hand another kind of polyimide made by conventional methods has poor applicability, but the liquid crystal alignment properties of its liquid crystal alignment layer are stable and independent from the rubbing times or layer thickness to obtain a large pretilt angle.

Therefore, a liquid crystal alignment layer forming agent comprised of polyimide block copolymer, having the above polyimides as block components in a molecule, can provide an excellent applicability and a resulting liquid crystal alignment layer is stable in liquid crystal alignment properties being independent from the rubbing times or layer thickness to obtain a large pretilt angle.

The properties of a high irradiation sensitivity and a high adhesive retention to substrate cannot be obtained together by conventional methods from polyimide homopolymer; polyimide block copolymer provides both properties at the same time, as a result, it can be possible to perform highly efficient alignment correction on the liquid crystal alignment layer.

Specifically, this alignment correction, implemented by irradiating, for example, ultraviolet light on a selected partial region of a thin layer of a liquid crystal alignment layer before or after alignment treatment such as rubbing, can be performed highly efficiently. Usually, adhesiveness of liquid crystal alignment layer to the substrate is lost by ultraviolet irradiation and the like, but in this case, excellent adhesiveness can be sustained. And, the liquid crystal alignment layer is not damaged during rubbing. Therefore, such liquid crystal alignment layer can provide an easy control of regional pretilt angle and also provide a highly efficient production of a liquid crystal display element having good contrast depending little on viewing angle.

Various applications of a thin layer comprised of a polyimide block copolymer of this invention include thin layers as an electrical insulator, a heat-resistant coating thin layer, a surface protection coating thin layer, and other thin layers. Especially it is useful as a liquid crystal alignment layer forming agent; the liquid crystal alignment layer comprised of polyimide block copolymer is especially suitable for producing liquid crystal alignment layers for STN type display elements or for TN type display elements.

A liquid crystal display element with a liquid crystal alignment layer formed from the thin layer forming agent of this invention is also suitable for a ferroelectric liquid crystal display element, if one selects an appropriate liquid crystal material filling between substrates.

Further, a liquid crystal display element formed from the thin layer forming agent of this invention is excellent in liquid crystal alignability and reliability and can be used effectively for various devices: especially, suitable for display devices such as calculator, watch, clock, digital board, word processor, personal computer, and liquid crystal television.

## Examples

Examples of this invention will be explained in detail below, but do not limit this invention.

In the examples below, a pretilt angle of a liquid crystal display element was measured by a crystal rotation method using He-Ne laser beam, according to the method described in T. J. Schffer, et al., Journal of Applied Physics., vol. 19, 2013 (1980).

Regarding the applicability of a thin layer forming agent, the thin layer thickness was measured by Alpha Step (U.S. TENCOR INSTRUMENTS CO. Product), a pin-contact type thickness measurement tool and an average thickness and its variation were measured.

Adhesiveness of a liquid crystal alignment layer to a substrate was evaluated by the occurrence of peeling after a rubbing treatment on a thin layer formed on a ITO layer.

The value of logarithmic viscosity number  $\eta_{1n}$  of each polymer was calculated by measuring the viscosity of a polymer solution of 0.5g/100ml in N-methyl-2-pyrrolidone at 30°C and by substituting the values into formula 1.

$$\eta_{1n} = \frac{1n \text{ (time for flowing-down of the solution/time for flowing-down for the solvent)}}{\text{(weight concentration of the polymer)}}$$



## Process Example 1

## Step 1

## 5 Preparation of a first polyamic acid prepolymer:

29.37g (131.0 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 14.55g (134.5 mmol) of p-phenylene-diamine were dissolved in 395.28g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a first polyamic acid prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyamic acid prepolymer was 0.10 dl/g.

## Step 2

## 15 Preparation of a second polyamic acid prepolymer:

2.39g (10.7 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 3.69g (7.1 mmol) of a diamine compound, which was indicated as compound A01 in Claim 16, were dissolved in 54.72g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a second polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the second polyamic acid prepolymer was 0.05 dl/g.

## Step 3

## 25 Preparation of a block copolymer type polyamic acid:

The entire solution of the first polyamic acid prepolymer which was obtained in step 1 and the entire solution of the second polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a block copolymer type polyamic acid having a logarithmic viscosity of 1.10 dl/g.

## Step 4

## Imidization:

20.00g of the block copolymer type polyamic acid which was obtained in step 3 was dissolved in 380g of N-methyl-2-pyrrolidone; further, 8.95g of pyridine and 11.57g of acetic anhydride were added and reacted for 5 hours at 110°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure; then a polyimide block copolymer with 1.10 dl/g of logarithmic viscosity was obtained. This is designated as Polymer 1.

## Process Example 2

## Step 1

## 45 Preparation of a first polyamic acid prepolymer:

28.87g (128.8 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 14.31g (132.3 mmol) of p-phenylene-diamine were dissolved in 388.62g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a first polyamic acid prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyamic acid prepolymer was 0.10 dl/g.

## Step 2

## 55 Preparation of a second polyamic acid prepolymer:

2.35g (10.5 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 4.48g (7.0 mmol) of a diamine compound, which was indicated as compound A07 in Claim 16 wherein the amino group in the benzene nucleus is in the para-position, were dissolved in 61.47g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to

obtain a solution of a second polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the second polyamic acid prepolymer was 0.05 dl/g.

### Step 3

Preparation of a block copolymer type polyamic acid:

The entire solution of the first polyamic acid prepolymer which was obtained in step 1 and the entire solution of the second polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a block copolymer type polyamic acid having a logarithmic viscosity of 1.08 dl/g.

### Step 4

Imidization:

20.00g of block copolymer type polyamic acid which was obtained in step 3 was dissolved in 380g of N-methyl-2-pyrrolidone; further, 8.81g of pyridine and 11.37g of acetic anhydride were added and reacted for 5 hours at 110°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure; then a polyimide block copolymer with 1.08 dl/g of logarithmic viscosity was obtained. This is designated as Polymer 2.

### Process Example 3

#### Step 1

Preparation of a first polyamic acid prepolymer

17.57g (78.4 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 10.18g (94.1 mmol) of p-phenylenediamine were dissolved in 249.75g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a first polyamic acid prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyamic acid prepolymer was 0.20 dl/g.

#### Step 2

Preparation of a second polyamic acid prepolymer:

10.56g (47.1 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 11.69g (31.4 mmol) of a diamine compound, which was indicated as compound A09 in Claim 16 wherein the recurring number a of methylene groups was 12 and the amino group in the benzene nucleus is in the para-position, were dissolved in 200.25g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a second polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the second polyamic acid prepolymer was 0.05 dl/g.

#### Step 3

Preparation of a block copolymer type polyamic acid:

The entire solution of the first polyamic acid prepolymer which was obtained in step 1 and the entire solution of the second polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a block copolymer type polyamic acid having a logarithmic viscosity of 1.50 dl/g.

## Step 4

## Imidization:

20.00g of block copolymer type polyamic acid which was obtained in step 3 was dissolved in 380g of N-methyl-2-pyrrolidone; further, 7.94g of pyridine and 10.25g of acetic anhydride were added and reacted for 5 hours at 110°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure; then a polyimide block copolymer with logarithmic viscosity of 1.66 dl/g was obtained. This is designated as Polymer 3.

## Process Example 4

## Step 1

## Preparation of a first polyamic acid prepolymer:

18.47g (82.4 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 10.70g (98.9 mmol) of p-phenylenediamine were dissolved in 262.53g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a first polyamic acid prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyamic acid prepolymer was 0.30 dl/g.

## Step 2

## Preparation of a second polyamic acid prepolymer:

11.10g (49.5 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 9.74g (33.0 mmol) of 3,5 - diamino - 4 - trifluoromethylbenzanilide were dissolved in 187.56g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a second polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the second polyamic acid prepolymer was 0.03 dl/g.

## Step 3

## Preparation of a block copolymer type polyamic acid:

The entire solution of the first polyamic acid prepolymer which was obtained in step 1 and the entire solution of the second polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a block copolymer type polyamic acid having logarithmic viscosity of 1.20 dl/g.

## Step 4

## Imidization:

20.00g of block copolymer type polyamic acid which was obtained in step 3 was dissolved in 380g of N-methyl-2-pyrrolidone; further, 8.35g of pyridine and 10.77g of acetic anhydride were added and reacted for 5 hours at 110°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure; then a polyimide block copolymer with logarithmic viscosity of 1.28 dl/g was obtained. This is designated as Polymer 4.

## Process Example 5

## Step 1

## Preparation of a first polyamic acid prepolymer:

23.64g (105.5 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 21.47g (108.3 mmol) of diaminodiphenylmethane were dissolved in 405.99g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temper-

ature to obtain a solution of a first polyamic acid prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyamic acid prepolymer was 0.10 dl/g.

#### Step 2

Preparation of a second polyamic acid prepolymer:

1.92g (8.6 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 2.97g (5.7 mmol) of a diamine compound, which was indicated as compound A01 in Claim 16, were dissolved in 44.01g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a second polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the second polyamic acid prepolymer was 0.04 dl/g.

#### Step 3

Preparation of a block copolymer type polyamic acid:

The entire solution of the first polyamic acid prepolymer which was obtained in step 1 and the entire solution of the second polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a block copolymer type polyamic acid having a logarithmic viscosity of 1.10 dl/g.

#### Step 4

Imidization:

20.00g of block copolymer type polyamic acid which was obtained in step 3 was dissolved in 380g of N-methyl-2-pyrrolidone; further, 7.22g of pyridine and 9.31g of acetic anhydride were added and reacted for 5 hours at 110°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure; then a polyimide block copolymer with logarithmic viscosity of 1.20 dl/g was obtained. This is designated as Polymer 5.

#### Process Example 6

#### Step 1

Preparation of a first polyamic acid prepolymer:

29.28g (130.6 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 13.76g (127.2 mmol) of p-phenylenediamine were dissolved in 387.36g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a first polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the first polyamic acid prepolymer was 0.10 dl/g.

#### Step 2

Preparation of a second polyamic acid prepolymer:

1.54g (6.9 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 5.41g (10.4 mmol) of a diamine compound, which was indicated as compound A01 in Claim 16, were dissolved in 121.32g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a second polyamic acid prepolymer having amino groups at its ends. The logarithmic viscosity of the second polyamic acid prepolymer was 0.04 dl/g.

#### Step 3

Preparation of a block copolymer type polyamic acid:

The entire solution of the first polyamic acid prepolymer which was obtained in step 1 and the entire solution of the second polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a block copolymer type polyamic acid having a logarithmic viscosity of 1.22 dl/g.

#### 5 Step 4

##### Imidization

20.00g of block copolymer type polyamic acid which was obtained in step 3 was dissolved in 380g of N-methyl-2-pyrrolidone; further, 8.70g of pyridine and 11.23g of acetic anhydride were added and reacted for 5 hours at 110°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure; then a polyimide block copolymer with 1.30 dl/g of logarithmic viscosity was obtained. This is designated as Polymer 6.

#### 15 Process Example 7

##### Step 1

##### Preparation of a first polyamic acid prepolymer:

17.45g (58.1 mmol) of 1, 3, 3a, 4, 5, 9b - hexahydro - 5 (tetrahydro - 2, 5 - dioxo - 3 - furanyl) naphtho [1,2 -c] furan - 1, 3 - dione, 6.63g (61.3 mmol) of p-phenylenediamine, and 1.68g (3.2 mmol) of a diamine compound, which was indicated as compound A01 in Claim 16, were dissolved in 231.84g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a first polyamic acid prepolymer having amino groups at its ends.

The logarithmic viscosity of the first polyamic acid prepolymer was 0.10 dl/g.

##### Step 2

##### Preparation of a second polyamic acid prepolymer:

15.92g (71.0 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride, 6.63g (61.3 mmol) of p-phenylenediamine, and 1.68g (3.2 mmol) of a diamine compound, which was indicated as compound A01 in Claim 16, were dissolved in 218.07g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a second polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the second polyamic acid prepolymer was 0.05 dl/g.

##### Step 3

##### Preparation of a block copolymer type polyamic acid:

The entire solution of the first polyamic acid prepolymer which was obtained in step 1 and the entire solution of the second polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a block copolymer type polyamic acid having a logarithmic viscosity of 1.08 dl/g.

##### Step 4

##### Imidization:

20.00g of block copolymer type polyamic acid which was obtained in step 3 was dissolved in 380g of N-methyl-2-pyrrolidone; further, 8.09g of pyridine and 10.44g of acetic anhydride were added and reacted for 5 hours at 110°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure; then a polyimide block copolymer with logarithmic viscosity of 1.10 dl/g was obtained. This is designated as Polymer 7.

## Process Example 8

## Step 1

## 5 Preparation of a first polyamic acid prepolymer:

29.08g (133.3 mmol) of pyromellitic acid dianhydride and 14.81g (137.0 mmol) of p-phenylenediamine were dissolved in 395.01g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a first polyamic acid prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyamic acid prepolymer was 0.10 dl/g.

## Step 2

## Preparation of a second polyamic acid prepolymer:

15 2.36g (10.8 mmol) of pyromellitic acid dianhydride and 3.75g (7.2 mmol) of a diamine compound, which was indicated as compound A01 in Claim 16, were dissolved in 54.99g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a second polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the second polyamic acid prepolymer was 0.05 dl/g.

## Step 3

## Preparation of a block copolymer type polyamic acid:

25 The entire solution of the first polyamic acid prepolymer which was obtained in step 1 and the entire solution of the second polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a block copolymer type polyamic acid having a logarithmic viscosity of 1.55 dl/g. This is designated as Polymer 8.

## Process Example 9

## Step 1

## 35 Preparation of a first polyamic acid prepolymer:

28.63g (127.7 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 14.58g (134.8 mmol) of p-phenylenediamine were dissolved in 388.89g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a first polyamic acid prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyamic acid prepolymer was 0.10 dl/g.

## Step 2

## Preparation of a second polyamic acid prepolymer:

45 3.10g (14.2 mmol) of pyromellitic acid dianhydride and 3.70g (7.1 mmol) of a diamine compound, which was indicated as compound A01 in Claim 16, were dissolved in 61.20g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a second polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the second polyamic acid prepolymer was 0.05 dl/g.

## Step 3

## Preparation of a block copolymer type polyamic acid:

55 The entire solution of the first polyamic acid prepolymer which was obtained in step 1 and the entire solution of the second polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a block copolymer type polyamic acid having a logarithmic viscosity of 1.30 dl/g. This is designated as Polymer 9.

## Process Example 10

## Step 1

## 5 Preparation of a first polyamic acid prepolymer:

5.19g (23.8 mmol) of pyromellitic acid dianhydride and 5.90 g (29.8 mmol) of 4, 4 - diaminodiphenylmethane were dissolved in 99.81g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a first polyamic acid prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyamic acid prepolymer was 0.10 dl/g.

## Step 2

## Preparation of a second polyamic acid prepolymer:

8.01g (35.7 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 5.90g (29.8 mmol) of 4, 4 - diaminodiphenylmethane were dissolved in 125.19g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a second polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the second polyamic acid prepolymer was 0.05 dl/g.

## Step 3

## Preparation of a block copolymer type polyamic acid:

The entire solution of the first polyamic acid prepolymer which was obtained in step 1 and the entire solution of the second polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C. Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a block copolymer type polyamic acid having a logarithmic viscosity of 1.10 dl/g.

## Step 4

## Imidization

25.00g of block copolymer type polyamic acid which was obtained in step 3 was dissolved in 475g of N-methyl-2-pyrrolidone; further, 9.42g of pyridine and 12.15g of acetic anhydride were added and reacted for 5 hours at 110°C. Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure; then a polyimide block copolymer with logarithmic viscosity of 1.10 dl/g was obtained. This is designated as Polymer 10.

## Process Example 11

## Step 1

## 45 Preparation of a first polyamic acid prepolymer:

5.35g (23.9 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 5.92g (29.9 mmol) of 4, 4 - diaminodiphenylmethane were dissolved in 101.43g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a first polyamic acid prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyamic acid prepolymer was 0.05 dl/g.

## Step 2

## Preparation of a second polyamic acid prepolymer:

7.81g (35.8 mmol) of pyromellitic acid dianhydride and 5.92g (29.9 mmol) of 4, 4 - diaminodiphenylmethane were dissolved in 123.57g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a second polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the second polyamic acid prepolymer was 0.10 dl/g.

Step 3

Preparation of a block copolymer type polyamic acid:

- 5 The entire solution of the first polyamic acid prepolymer which was obtained in step 1 and the entire solution of the second polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C. Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a block copolymer type polyamic acid having a logarithmic viscosity of 1.10 dl/g. This is designated as Polymer 11.

10 Process Example 12

Step 1

- 15 Preparation of a first polyamic acid prepolymer:

9.77g (44.8 mmol) of pyromellitic dianhydride and 4.27g (37.5 mmol) of 1, 4 - diaminocyclohexane were dissolved in 126.36g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a first polyamic acid prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyamic acid prepolymer was 0.12 dl/g.

Step 2

Preparation of a second polyamic acid prepolymer:

- 25 6.70g (29.9 mmol) of 2, 3, 5- tricarboxycyclopentylacetic dianhydride and 4.27g (37.5 mmol) of 1, 4 - diaminocyclohexane were dissolved in 98.73g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a second polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the second polyamic acid prepolymer was 0.06 dl/g.

30 Step 3

Preparation of a block copolymer type polyamic acid:

- 35 The entire solution of the first polyamic acid prepolymer which was obtained in step 1 and the entire solution of the second polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C. Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a block copolymer type polyamic acid having a logarithmic viscosity of 1.14 dl/g.

40 Step 4

Imidization:

- 45 25.00g of block copolymer type polyamic acid which was obtained in step 3 was dissolved in 475g of N-methyl-2-pyrrolidone; further, 11.82g of pyridine and 15.25g of acetic anhydride were added and reacted for 5 hours at 110°C. Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure; then a polyimide block copolymer with 1.14 dl/g of logarithmic viscosity was obtained. This is designated as Polymer 12.

50 Process Example 13

Step 1

- 55 Preparation of a first polyamic acid prepolymer:

7.21g (32.2 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 7.65g (38.6 mmol) of 4, 4 - diaminodiphenylmethane were dissolved in 133.74g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temper-



ature to obtain a solution of a first polyamic acid prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyamic acid prepolymer was 0.16 dl/g.

## Step 2

Preparation of a second polyamic acid prepolymer:

7.21g (32.2 mmol) of tricarboxycyclopentylacetic dianhydride and 2.94g (25.7 mmol) of 1, 4 - diaminocyclohexane were dissolved in 98.73g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a second polyamic acid prepolymer having carboxylic anhydride groups in its ends. The logarithmic viscosity of the second polyamic acid prepolymer was 0.06 dl/g.

## Step 3

Preparation of a block copolymer type polyamic acid:

The entire solution of the first polyamic acid prepolymer which was obtained in step 1 and the entire solution of the second polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a block copolymer type polyamic acid having a logarithmic viscosity of 1.19 dl/g

## Step 4

Imidization:

25.00g of block copolymer type polyamic acid which was obtained in step 3 was dissolved in 475g of N-methyl-2-pyrrolidone; further, 10.17g of pyridine and 13.13g of acetic anhydride were added and reacted for 5 hours at 110°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure; then a polyimide block copolymer with 1.19 dl/g of logarithmic viscosity was obtained. This is designated as Polymer 13.

## Process Example 14

### Step 1

Preparation of a first polyimide prepolymer:

29.37g (131.0 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 13.78g (127.4 mmol) of p-phenylene-diamine were dissolved in 395.28g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature; further, 20.73g of pyridine and 26.74g of acetic anhydride were added and reacted at 60°C for 6 hours. Then 0.77g (7.1mmol) of p-phenylenediamine added and reacted for 4 hours to obtain a first polyimide prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyimide prepolymer was 0.30 dl/g.

### Step 2

Preparation of a second polyimide prepolymer:

2.39g (10.7 mmol) of 2,3,5- tricarboxycyclopentylacetic dianhydride and 3.69g (7.1 mmol) of a diamine compound, which was indicated as compound A01 in Claim 16, were dissolved in 54.72g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature; further, 0.56g of pyridine and 0.78g of acetic anhydride were added and reacted at 60°C for 6 hours to obtain a second polyimide prepolymer having carboxylic anhydride group at its ends. The logarithmic viscosity of the second polyimide prepolymer was 0.20 dl/g.

## Step 3

Preparation of a polyimide block copolymer:

The entire solution of the first polyimide prepolymer which was obtained in step 1 and the entire solution of the second polyimide prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a polyimide block copolymer having a logarithmic viscosity of 1.10 dl/g. This is designated as Polymer 14.

## Process Example 15

## Step 1

Preparation of a first polyimide prepolymer:

33.29g (90.9 mmol) of pyromellitic acid tetraethyl ester and 10.38g (95.9 mmol) of 4, 4 - diaminodiphenylmethane were dissolved in 393.03g of N-methyl-2-pyrrolidone and reacted with stirring for 6 hours at 150°C to obtain a solution of a first polyimide prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyimide prepolymer was 0.02 dl/g.

## Step 2

Preparation of a second polyimide prepolymer:

3.70g (10.1 mmol) of pyromellitic acid tetraethyl ester and 2.63g (5.1 mmol) of a diamine compound, which was indicated as compound A01 in Claim 16, were dissolved in 56.1 g of N-methyl-2-pyrrolidone and reacted with stirring for 6 hours at 150°C to obtain a solution of a second polyimide prepolymer having ethylester groups at its ends. The logarithmic viscosity of the second polyimide prepolymer was 0.02 dl/g.

## Step 3

Preparation of a polyimide block copolymer:

The entire solution of the first polyimide prepolymer which was obtained in step 1 and the entire solution of the second polyimide prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 150°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a polyimide block copolymer having a logarithmic viscosity of 0.20 dl/g. This is designated as Polymer 15.

## Process Example 16

## Step 1

Preparation of a first polyimide prepolymer:

21.02g (93.8mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 24.24g (96.8 mmol) of diphenylmethane - 4, 4 - diisocyanate were dissolved in 407.34g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a first polyimide prepolymer having isocyanate groups at its ends. The logarithmic viscosity of the first polyimide prepolymer was 0.10 dl/g.

## Step 2

Preparation of a second polyimide prepolymer

1.83g (8.2 mmol) of 2,3,5- tricarboxycyclopentylacetic dianhydride and 2.92g (5.1 mmol) of a diisocyanate compound, which was indicated as compound B01 above, were dissolved in 42.75g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a second polyimide prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the second polyimide prepolymer was 0.05 dl/g.

## Step 3

Preparation of a polyimide block copolymer:

The entire solution of the first polyimide prepolymer which was obtained in step 1 and the entire solution of the second polyimide prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a polyimide block copolymer having a logarithmic viscosity of 1.10 dl/g. This is designated as Polymer 16.

## Process Example 17

## Step 1

Preparation of a polyimide prepolymer:

0.96g (4.3 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 4.10g (7.2 mmol) of a diisocyanate compound, which was indicated as compound B01 above, were dissolved in 45.54g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a polyimide prepolymer having isocyanate groups at its ends. The logarithmic viscosity of the polyimide prepolymer was 0.10 dl/g.

## Step 2

Preparation of a second polyamic acid prepolymer:

30.25g (138.7 mmol) of pyromellitic dianhydride and 14.69g (135.8 mmol) of p-phenylenediamine were dissolved in 404.46g of N-methyl-2-pyrrolidone and reacted with stirring for 6 hours at room temperature to obtain a solution of a polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the polyamic acid prepolymer was 0.10 dl/g.

## Step 3

Preparation of a polyimide-polyamic acid block copolymer:

The entire solution of the polyimide prepolymer which was obtained in step 1 and the entire solution of the polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a polyimide-polyamic acid block copolymer having a logarithmic viscosity of 1.10 dl/g. This is designated as Polymer 17.

## Process Example 18

## Step 1

Preparation of a polyimide prepolymer:

2.44g (11.0 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 4.14g (7.1 mmol) of a diisocyanate compound, which was indicated as compound B01 above, were dissolved in 59.22g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a polyimide prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the polyimide prepolymer was 0.10 dl/g.

## Step 2

Preparation of a polyamic acid prepolymer:

28.75g (131.8 mmol) of pyromellitic dianhydride and 14.67g (135.7 mmol) of p-phenylenediamine were dissolved in 390.78g of N-methyl-2-pyrrolidone and reacted with stirring for 6 hours at room temperature to obtain a solution of a polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the polyamic acid prepolymer was 0.10 dl/g.

## Step 3

## Preparation of a polyimide-polyamic acid block copolymer

5 The entire solution of the polyimide prepolymer which was obtained in step 1 and the entire solution of the polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a polyimide-polyamic acid block copolymer having a logarithmic viscosity of 1.11 dl/g. This is designated as Polymer 18.

## Process Example 19

## Step 1

## 15 Preparation of a polyimide prepolymer:

1.13g (4.3 mmol) of pyromellitic acid tetraethyl ester and 3.75g (7.2 mmol) of a diamine compound illustrated as A01 in Claim 16 were dissolved in 34.29g of N-methyl-2-pyrrolidone and reacted for 6 hours at 150°C to obtain a solution of a first polyimide prepolymer having amino groups at its ends. The logarithmic viscosity of the first polyimide prepolymer was 0.10 dl/g.

## Step 2

## Preparation of a polyamic acid prepolymer:

25 31.37g (140.1 mmol) of 2,3,5-tricarboxycyclopentylacetic dianhydride and 14.81g (137.1 mmol) of p-phenylenediamine were dissolved in 415.62g of N-methyl-2-pyrrolidone and reacted with stirring for 2 hours at room temperature to obtain a solution of a polyamic acid prepolymer having carboxylic anhydride groups at its ends. The logarithmic viscosity of the polyamic acid prepolymer was 0.10 dl/g.

## Step 3

## Preparation of a polyimide-polyamic acid block copolymer:

35 The entire solution of the polyimide prepolymer which was obtained in step 1 and the entire solution of the polyamic acid prepolymer which was obtained in step 2 were mixed and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a polyimide-polyamic acid block copolymer having a logarithmic viscosity of 1.20 dl/g. This is designated as Polymer 19.

## Comparative Process Example 1

45 In Comparative Process Example 1, the same kind and the same amount to the total amount of tetracarboxylic dianhydride as in steps 1 and 2 of Process Example 1 and the same kinds and the same amounts of two diamine compounds as in the same steps were gathered (mixed) and reacted together. A polyamic acid was prepared in this reaction (method), and then was imidized as in step 4 of Process Example 1 to obtain a polyimide.

Preparation of a polyamic acid

50 31.76g (141.7 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride, 14.55g (134.5 mmol) of p-phenylenediamine, and 3.69g (7.1 mmol) of a diamine compound, which was indicated as compound A01 in Claim 16, were dissolved in 450.00g of N-methyl-2-pyrrolidone and reacted with stirring for 6 hours at 60°C.

55 Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a hybrid type polyamic acid having a logarithmic viscosity of 1.23 dl/g.

## Imidization:

20.00g of the hybrid polyamic acid was dissolved in 380g of N-methyl-2-pyrrolidone; further, 8.96g of pyridine and 11.57g of acetic anhydride were added and reacted for 5 hours at 110°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a hybrid type polyimide copolymer having a logarithmic viscosity of 1.25 dl/g. This is designated as Comparative Polymer 1.

## Comparative Process Example 2

In Comparative Process Example 2, two kinds of polyimide mixtures below were produced following the manner of Process Example 1.

## (1) A first polyimide

The same kinds of tetracarboxylic dianhydride and diamine compound as the ones used in step 1 of Process Example 1 were reacted in equivalent amounts to prepare a polyamic acid; further, the imidization was performed in the same manner as in step 4 of Process Example 1 to obtain a polyimide.

## (2) A second polyimide

The same kinds of tetracarboxylic dianhydride and diamine compound as the ones used in step 2 of Process Example 1 were reacted with stirring in equivalent amounts to prepare a polyamic acid; further, the imidization was performed in the same manner as in step 4 of Process Example 1 to obtain a polyimide.

## Preparation of a polyamic acid:

15.05g (67.1 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 34.95g (67.1 mmol) of a diamine compound, which was indicated as compound A01 in Claim 16, were dissolved in 450.00g of N-methyl-2-pyrrolidone and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a polyamic acid having a logarithmic viscosity of 0.77 dl/g.

## Imidization:

20.00g of the above polyamic acid was dissolved in 380g of N-methyl-2-pyrrolidone; further, 4.25g of pyridine and 5.48g of acetic anhydride were added and reacted for 5 hours at 110°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a first polyimide having a logarithmic viscosity of 0.77 dl/g.

## Preparation of a polyamic acid:

33.73g (150.5 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride and 16.27g (150.5 mmol) of p-phenylene-diamine were dissolved in 450.00g of N-methyl-2-pyrrolidone and reacted with stirring for 6 hours at 60°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a polyamic acid having a logarithmic viscosity of 1.30 dl/g.

## Imidization:

20.00g of the above polyamic acid was dissolved in 380g of N-methyl-2-pyrrolidone; further, 9.51g of pyridine and 12.29g of acetic anhydride were added and reacted while the mixture was being stirred for 5 hours at 110°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a second polyimide having a logarithmic viscosity of 1.25 dl/g.

Preparation of a polyimide mixture:

10.6 weight % of the first polyimide and 89.4 weight % of the second polyimide which were obtained in the above manner were mixed to produce a polyimide mixture having the same monomer composition as in the Polymer 1 of Process Example 1. This is designated as Comparative polymer 2.

Comparative Process Example 3

In Comparative Process Example 3, an excess amount of tetracarboxylic dianhydride was reacted with a diamine compound; further, another kind of diamine compound was added and reacted with remained tetracarboxylic dianhydride to prepare polyamic acid. Further, imidization was performed to produce a polyimide.

Preparation of a polyamic acid:

14.55g (134.5 mmol) of p-phenylenediamine was dissolved in 450.00g of N-methyl-2-pyrrolidone and kept at 0°C in ice bath; further, 31.76g (141.7 mmol) of 2,3,5 - tricarboxycyclopentylacetic dianhydride was gradually added and stirred for 3 hours in ice bath. 3.69g (7.1 mmol) of a diamine compound which was indicated as a compound A01 in Claim 16 and 2.24g (28.3 mmol) of pyridine were added to the solution and reacted with stirring for 3 hours.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a polyamic acid having a logarithmic viscosity of 0.45 dl/g.

Imidization

20.00g of the above polyamic acid was dissolved in 380g of N-methyl-2-pyrrolidone; further, 8.96g of pyridine and 11.57g of acetic anhydride were added and reacted for 5 hours at 110°C.

Resulting reaction product was poured into a large excess of methyl alcohol to precipitate a polymer; the solid was separated, rinsed with methyl alcohol, and dried for 15 hours at 40°C under reduced pressure to obtain a modified-type polyimide copolymer having a logarithmic viscosity of 0.50 dl/g. This is designated as Comparative Polymer 3.

Example 1

The Polymer 1 which was obtained in Process Example 1 was dissolved in  $\gamma$ -butyrolactone to obtain a solution with 5 weight % solids concentration; the solution was filtered through a 1  $\mu$ m pore diameter filter to produce a thin layer forming agent.

The obtained thin layer forming agent was used as a liquid crystal alignment layer forming agent and was applied by the printing method to one side of a glass substrate on which a transparent ITO conductive layer was formed. The substrate was heat dried at 180°C for 1 hour to obtain a thin layer. As shown in Table 1, measurement of the thickness was 600Å in average with  $\pm 20$ Å variation, demonstrating excellent thickness uniformity.

A rubbing machine was equipped with a roller wound with a nylon cloth. The thin layer was rubbed at the pile contact length of 0.6mm, roller rotation speed of 500rpm, and stage feed movement rate of 1 cm/sec to obtain a thin liquid crystal alignment layer. This liquid crystal alignment layer demonstrated excellent adhesiveness to the substrate. No peeling phenomenon from the substrate by rubbing was observed.

Example 2

The same thin layer forming agent as in Example 1 was applied on the surface of the same glass substrate as above to have 800Å of thickness after drying by a spinner and was dried for 1 hour at 180°C to form a thin layer. Measurement of the thickness showed 800Å in average with  $\pm 20$ Å of variation, demonstrating excellent thickness uniformity.

The same rubbing treatment as in Example 1 was performed on the thin layer to obtain a liquid crystal alignment layer demonstrating excellent adhesiveness to the substrate. No peeling phenomenon from the substrate by rubbing was observed.

On peripheries of each of the two substrates obtained above, epoxy resin containing 17  $\mu$ m diameter aluminum oxide particles was screen printed. Then, the two substrates were positioned face to face via the gap between them so that the rubbing direction on each liquid crystal alignment layer is reverse-paralleled. The peripheries of the substrates were contacted and pressed, and the adhesive was hardened.

Then, nematic type liquid crystal "MLC-2001" (Merck) was injected into the cell gap between the opposite substrate surfaces and the adhesive agent on their peripheries, and the inlet was sealed by the epoxy type adhesive agent to form a liquid crystal cell. Further, on outer surfaces of both substrates that constitute the liquid crystal cell, polarizers were

attached so that the polarizing direction remains in accordance with the rubbing direction of the liquid crystal alignment layer on one side of the substrate surface. Thus, the liquid crystal display element was produced.

As shown in Table 2, alignment properties of the liquid crystal molecule in the liquid crystal display element was excellent and the pretilt angle was 5.3°.

#### Examples 3 - 20

Using polymers 2 - 19, which were prepared respectively in Process Examples 2 - 19, in place of polymer 1, thin layer forming agents were prepared in the same manner as in Example 1; using each thin layer forming agent, a thin layer was respectively formed on the surface of the glass substrate for liquid crystal display elements in the same manner as in Example 1 and the average and the variation of thickness for each thin layer were measured. And, in the cases of Polymer 8, Polymer 9 and Polymer 11, imidization was performed by heating at 180°C after applying and drying. Table 1 shows the results.

Rubbing treatment was performed on each of the formed layers using the same conditions as in Example 1 to obtain a liquid crystal alignment layer demonstrating excellent adhesiveness to the substrate and no peeling from substrate by rubbing was observed.

#### Comparative Example 1

Using Comparative Polymer 1, a hybrid type polyimide copolymer, obtained in Comparative Process Example 1, a thin layer forming agent was prepared in the same manner as in Example 1, and a thin layer was formed in the same manner as in Example 1. As shown in Table 1, measurement of the thickness showed 630Å in average with  $\pm 80\text{Å}$  of variation, demonstrating poor thickness uniformity.

Rubbing treatment was performed on the layer surface in the same manner as in Example 1 to form a liquid crystal alignment layer. And no peeling from substrate was observed.

#### Comparative Example 2

Using Comparative Polymer 2, a polyimide mixture, obtained in Comparative Process Example 2, a thin layer forming agent was prepared in the same manner as in Example 1, and a thin layer was formed in the same manner as in Example 1. As shown in Table 1, measurement of the thickness showed 760Å in average with  $\pm 150\text{Å}$  of variation, demonstrating very poor thickness uniformity and showing a surface with a mottled pattern.

Rubbing treatment was performed on the thin layer surface in the same manner as in Example 1 to form a liquid crystal alignment layer; minute rubbing scratches on the surface were observed.

#### Comparative Example 3

Using Comparative Polymer 3, a modified-type polyimide, obtained in the Comparative Process Example 3, a thin layer forming agent was prepared in the same manner as in Example 1, and a thin layer was formed in the same manner as in Example 1. As shown in Table 1, measurement of the thickness showed 580Å in average with  $\pm 50\text{Å}$  of variation, demonstrating poor thickness uniformity.

Rubbing treatment was performed on the layer surface in the same manner as in Example 1 to form a liquid crystal alignment layer. And no peeling from substrate by rubbing was observed.

It is obvious from Table 1 that the liquid crystal alignment layers, obtained from the thin layer forming agents with Polymers 1 - 19 of polyimide-type block copolymers, have a very small variation in thickness within the range of  $\pm 10\text{Å}$  to  $\pm 25\text{Å}$ . This is because the thin layer forming agent for each liquid crystal alignment layer can provide excellent and uniform applicability, by which excellent liquid crystal alignment layers were formed.

It is obvious from Example 8, Example 9, and Example 11 that even block copolymer type polyamic acids used as polyimide-type block copolymers show excellent properties like polyimide block copolymers show.

#### Example 21

Using the thin layer forming agent prepared in Example 1, a thin layer was formed on a glass substrate surface in the same manner as in Example 2. Measurement of the thickness showed 500Å on average with  $\pm 20\text{Å}$  of variation, demonstrating excellent thickness uniformity.

With all conditions equal to Example 1, except that the rubbing times was performed twice on the thin layer surface, a liquid crystal alignment layer was produced. The liquid crystal alignment layer demonstrated excellent adhesiveness to the substrate and no peeling from substrate by rubbing was observed.

Using two substrates having a liquid crystal alignment layer obtained in such a manner, a liquid crystal display element was produced in the same manner as in Example 2. As shown in Table 2, alignment properties of the liquid crystal molecule in the liquid crystal display element were excellent and the pretilt angle was 5.0°.

It is obvious that the liquid crystal alignment layer, even with multiple rubbing treatments, maintains as excellent adhesiveness and alignment properties as it does with one rubbing treatment. In other words, the liquid crystal alignment layer obtains stable adhesiveness and alignment properties.

#### Example 22 - 53

Thin layer forming agents with Polymers 1 - 9 and with Polymers 14 - 19 were prepared as liquid crystal alignment layer forming agents. Thin layers of various thickness within the range of 500Å to 1500Å were formed. A variety of liquid crystal display elements were produced as in Example 21, except that the rubbing times was selected from 1 to 5. The alignment properties and the pretilt angle of the liquid crystal molecule in each of liquid crystal display elements were measured. With polymers 8 and 9, the thin layer was applied and dried, then heated at 180°C for imidization. Table 2 and Table 3 show the results.

According to Examples 21 - 53, it was obvious that obtained liquid crystal alignment layers had nearly constant pretilt angles such as 5.0°, 5.1°, and 5.2° with twice rubbing treatments even thickness was varied within the range of 500Å to 1500Å. It is understood that these liquid crystal alignment layers gave very stable pretilt angles in the wide range of layer thickness, being little affected by fluctuations of the production process conditions.

According to Example 2, Example 24, and Example 25, it is understandable that, with all other conditions equal except the rubbing times, nearly the same pretilt angles were obtained at each rubbing time from 1 through 5. Yet obtained alignment properties at each stage were excellent.

The similar results as above were confirmed in other examples where different kinds of polyimide-type block copolymer were used.

#### Comparative Examples 4 - 21

Using the thin layer forming agent as prepared in Comparative Examples 1 - 3 as a liquid crystal alignment layer forming agent, thin layers of various thickness were formed within the range of 500Å to 1500Å. With all other conditions remained equal as in Example 21, except that the rubbing times was selected from 1 to 5, a variety of liquid crystal display element for reference were produced. Then, alignment properties and pretilt angles of liquid crystal molecules were measured for each liquid crystal display element. Table 4 shows the results.

#### Reference Example 1

Using the first polyimide obtained in Comparative Process Example 2, a thin layer forming agent was prepared; then, a thin layer was formed as in Example 1. As shown in Table 1, the thickness was 810Å on average with ±80Å variation, demonstrating very poor layer thickness uniformity.

The rubbing treatment was performed on this layer surface as in Example 1 to form a liquid crystal alignment layer; minute rubbing scratches on the surface were observed.

#### Reference Example 2

Using the second polyimide obtained in Comparative Process Example 2, a thin layer forming agent was prepared; then, a thin layer was formed as in Example 1. As shown in Table 1, measurement of the thickness showed 800Å on average with ±20Å variation, demonstrating excellent thickness uniformity.

Rubbing treatment was performed on this layer surface in the same manner as in Example 1 to form a liquid crystal alignment layer. No rubbing scratches on the surface were observed.

#### Reference Examples 3 - 8

Using the same thin layer forming agent of Reference Example 1 that contains the first polyimide obtained in Comparative Process Example 2 as a liquid crystal alignment layer forming agent, thin layers of various thickness were formed within the range of 500Å to 1500Å. With all other conditions remained equal as in Example 21, except that the rubbing times was selected from 1 to 5, a variety of liquid crystal display elements for reference were produced. Then, alignment properties and pretilt angles of liquid crystal molecules were measured for each liquid crystal display element. Table 5 shows the results.



## Reference Examples 9 - 14

Using the same thin layer forming agent of Reference Example 2 that contains the second polyimide obtained in Comparative Example 2 as a liquid crystal alignment layer forming agent, thin layers of various thickness were formed within the range of 500Å to 1500Å. With all other conditions remained equal as in Example 21, except that the rubbing times was selected from 1 to 5, a variety of liquid crystal display elements for reference were produced. Then, alignment properties and pretilt angles of liquid crystal molecules were measured for each liquid crystal display element. Table 5 shows the results.

According to the results of Comparative Examples 4 - 21, it is obvious that, even with the polyimide of the same monomer composition, such excellent properties derived from block copolymer could not be obtained when the polymer that constituted the liquid crystal alignment layer was a hybrid type (Comparative Polymer 1) or a simple mixture (Comparative Polymer 2), not a block copolymer.

It was understood, according to Comparative Examples 4 - 7 and others, that even though the rubbing times was the same, the pretilt angles were changed dramatically when the thickness was changed; according to Comparative Examples 8 and 9, even though the layer thickness was the same, the pretilt angles were dramatically changed when the times for rubbing treatment was changed.

According to Comparative Examples 10 - 13 and others, it is understood that alignment properties obtained were poor even though the times for rubbing was the same because the pretilt angle was dramatically changed when the thickness was changed; according to Comparative Examples 14, 15, and others, it is understood that the pretilt angle was small even though the thickness was constant and alignment properties were greatly affected by the times for rubbing even though the thickness was the same.

Further, according to Reference Examples 1 and 3 - 8, it is obvious that with the first polyimide of homopolymer, the applicability of liquid crystal alignment layer and its adhesiveness to the substrate were poor while a very large pretilt angle was obtained. However, with changes in the thickness or the rubbing times, the pretilt angle changed dramatically.

According to Reference Examples 2 and 9 - 14, when the second polyimide of homopolymer was used, it is obvious that both applicability of the liquid crystal alignment layer and its adhesiveness to the substrate were excellent but a large pretilt angle could not be obtained.

Therefore, it is understood that the polyimide homopolymer with recurring units of each block component that constitutes a polyimide block copolymer is unable to have plural excellent properties together as a polyimide block copolymer does.

Table 1

Number	Polymer	Layer Thickness (Å)		Adhesiveness
		average	variety	
Example 1	Polymer 1	600	$\pm 20$	excellent
Example 3	Polymer 2	600	$\pm 15$	excellent
Example 4	Polymer 3	620	$\pm 10$	excellent
Example 5	Polymer 4	640	$\pm 20$	excellent
Example 6	Polymer 5	660	$\pm 15$	excellent
Example 7	Polymer 6	500	$\pm 25$	excellent
Example 8	Polymer 7	610	$\pm 15$	excellent
Example 9	Polymer 8	650	$\pm 20$	excellent
Example 10	Polymer 9	660	$\pm 15$	excellent
Example 11	Polymer 10	600	$\pm 15$	excellent
Example 12	Polymer 11	620	$\pm 10$	excellent
Example 13	Polymer 12	640	$\pm 20$	excellent
Example 14	Polymer 13	660	$\pm 15$	excellent
Example 15	Polymer 14	600	$\pm 15$	excellent
Example 16	Polymer 15	600	$\pm 20$	excellent
Example 17	Polymer 16	620	$\pm 10$	excellent
Example 18	Polymer 17	630	$\pm 20$	excellent
Example 19	Polymer 18	650	$\pm 15$	excellent
Example 20	Polymer 19	600	$\pm 10$	excellent
Comparative Example 1	Comparative Polymer 1	630	$\pm 80$	excellent
Comparative Example 2	Comparative Polymer 2	760	$\pm 150$	poor
Comparative Example 3	Comparative Polymer 3	580	$\pm 50$	poor
Referential Example 1	First Polyimide of Comparative Process Example 2	810	$\pm 80$	poor
Referential Example 2	Second Polyimide of Comparative Process Example 2	800	$\pm 20$	excellent

Table 2

Number	Polymer	Layer Thickness (Å)	Rubbing (times)	Pretilt Angle (°)	Alignment Properties
Example 2	Polymer 1	800	1	5.3	excellent
Example 21	Polymer 1	500	2	5.0	excellent
Example 22	Polymer 1	1000	2	5.1	excellent
Example 23	Polymer 1	1500	2	5.2	excellent
Example 24	Polymer 1	800	1	5.3	excellent
Example 25	Polymer 1	800	5	5.2	excellent
Example 26	Polymer 2	800	2	4.5	excellent
Example 27	Polymer 2	500	2	4.4	excellent
Example 28	Polymer 2	800	5	4.5	excellent
Example 29	Polymer 3	800	2	3.4	excellent
Example 30	Polymer 3	500	2	3.3	excellent
Example 31	Polymer 3	800	5	3.4	excellent
Example 32	Polymer 4	800	2	6.0	excellent
Example 33	Polymer 4	500	2	6.4	excellent
Example 34	Polymer 4	800	5	6.3	excellent
Example 35	Polymer 5	800	2	3.0	excellent
Example 36	Polymer 6	800	2	3.5	excellent

Table 3

Number	Polymer	Layer Thickness (Å)	Rubbing (times)	Pretilt Angle(°)	Alignment Properties
Example 37	Polymer 7	500	2	4.0	excellent
Example 38	Polymer 7	800	2	3.8	excellent
Example 39	Polymer 7	1500	2	3.9	excellent
Example 40	Polymer 7	800	1	4.1	excellent
Example 41	Polymer 7	800	5	3.9	excellent
Example 42	Polymer 8	800	2	7.0	excellent
Example 43	Polymer 9	800	2	6.5	excellent
Example 44	Polymer 14	800	2	3.4	excellent
Example 45	Polymer 15	800	2	6.5	excellent
Example 46	Polymer 16	500	2	3.0	excellent
Example 47	Polymer 16	800	2	3.2	excellent
Example 48	Polymer 16	1500	2	3.0	excellent
Example 49	Polymer 16	800	1	3.1	excellent
Example 50	Polymer 16	800	5	3.0	excellent
Example 51	Polymer 17	800	2	7.8	excellent
Example 52	Polymer 18	800	2	7.2	excellent
Example 53	Polymer 19	800	2	4.8	excellent

Table 4

Number	Polymer	Layer Thickness (Å)	Rubbing (times)	Pretilt Angle (°)	Alignment Properties
Comparative Example 4	Comparative Polymer 1	500	2	3.2	excellent
Comparative Example 5	Comparative Polymer 1	800	2	4.5	excellent
Comparative Example 6	Comparative Polymer 1	1000	2	6.5	excellent
Comparative Example 7	Comparative Polymer 1	1500	2	7.0	excellent
Comparative Example 8	Comparative Polymer 1	800	1	8.0	excellent
Comparative Example 9	Comparative Polymer 1	800	5	2.2	excellent
Comparative Example 10	Comparative Polymer 2	500	2	2.1	excellent
Comparative Example 11	Comparative Polymer 2	800	2	3.0	excellent
Comparative Example 12	Comparative Polymer 2	1000	2	-	poor
Comparative Example 13	Comparative Polymer 2	1500	2	-	poor
Comparative Example 14	Comparative Polymer 2	800	1	-	poor
Comparative Example 15	Comparative Polymer 2	800	5	2.1	excellent
Comparative Example 16	Comparative Polymer 3	500	2	-	poor
Comparative Example 17	Comparative Polymer 3	800	2	-	poor
Comparative Example 18	Comparative Polymer 3	1000	2	-	poor
Comparative Example 19	Comparative Polymer 3	1500	2	-	poor
Comparative Example 20	Comparative Polymer 3	800	1	-	poor
Comparative Example 21	Comparative Polymer 3	800	5	-	poor

Table 5

Number	Polymer	Layer Thickness (Å)	Rubbing (times)	Pretilt Angle (°)
Referential Example 3	First Polyimide of Comparative Process Example 2	500	2	60
Referential Example 4	First Polyimide of Comparative Process Example 2	800	2	80
Referential Example 5	First Polyimide of Comparative Process Example 2	1000	2	80
Referential Example 6	First Polyimide of Comparative Process Example 2	1500	2	89
Referential Example 7	First Polyimide of Comparative Process Example 2	800	1	89
Referential Example 8	First Polyimide of Comparative Process Example 2	800	5	50
Referential Example 9	Second Polyimide of Comparative Process Example 2	500	2	0.8
Referential Example 10	Second Polyimide of Comparative Process Example 2	800	2	1.0
Referential Example 11	Second Polyimide of Comparative Process Example 2	1000	2	1.2
Referential Example 12	Second Polyimide of Comparative Process Example 2	1500	2	1.5
Referential Example 13	Second Polyimide of Comparative Process Example 2	800	1	1.5
Referential Example 14	Second Polyimide of Comparative Process Example 2	800	5	0.9

## Example 54

Using the thin layer forming agent prepared in Example 1, a thin layer was formed on a glass substrate to form a liquid crystal alignment layer with 800Å of the thickness. Ultraviolet rays were irradiated to this thin layer at 3J/cm<sup>2</sup> by a low-pressure mercury lamp. Rubbing treatment was performed on the substrate in the same manner as in Example 21 to produce liquid crystal display elements. Alignment properties of the liquid molecules in this liquid crystal display element were excellent and the pretilt angle was 0.5°

It is obvious from this result that the liquid crystal alignment layer formed from the thin layer related to Example 21 provides a small pretilt angle after irradiation of ultraviolet rays, then a modification of alignment properties can be effectively made.

EFFECTS OF THE INVENTION

In the process of producing a block copolymer type polyamic acid of this invention, plural kinds of reactive polyamic acid prepolymers, which have reactive groups originating from a tetracarboxylic component and amino groups reacting with the reactive group, and have a different molecular structure of recurring units from each other, are prepared; and further, reacted with stirring to be comprised of plural polyamic acid block components which have different molecular structures of recurring units from each other; thus, a block copolymer type polyamic acid is produced having coexisting properties derived from each of the block components. In this process, it is easy to sufficiently control conditions in each polycondensation reaction, so that block copolymer type polyamic acid having expected properties can be produced with certainty. By imidization, the block copolymer type polyamic acid becomes a polyimide block copolymer having coexisting excellent properties of each of the polyimide block components; therefore, a polyimide having coexisting excellent properties from each of the block components is obtained: for example, the applicability, alignment controllability; pretilt angle, rubbing scratch resistivity, voltage retention rate, resistance of uninsulation, flicker resistivity, and retention stability necessary for liquid crystal alignment layer.

In the process of producing a polyimide block copolymer of this invention, plural kinds of reactive polyimides, which have reactive groups originating from a tetracarboxylic component and amino groups or isocyanate groups reacting with the reactive group, and have a different molecular structure of recurring units from each other, are prepared; and further, reacted with stirring to be comprised of plural polyimide block components which have different molecular structures of recurring units from each other; thus, a polyimide block copolymer having coexisting properties derived from each of the block components is produced. In this process, it is easy to sufficiently control conditions in each polycondensation reaction, so that the polyimide block copolymer having expected properties can be produced with certainty. The polyimide block copolymer becomes one having coexisting excellent properties of each of the polyimide block components; therefore, a polyimide can be prepared having excellent plural properties which are difficult to be obtained at the same time by conventional methods, for example, the necessary properties above mentioned for liquid crystal alignment layer.

In the process of producing a polyimide-polyamic acid block copolymer of this invention, plural kinds of reactive polyimide prepolymers and plural reactive polyamic acid prepolymers, each of which has reactive groups originating from a tetracarboxylic component, and amino groups or isocyanate groups reacting with the reactive groups, and have a different molecular structure of recurring unit from each other, are prepared; and further, reacted with stirring to be comprised of plural polyimide block components and plural polyamic acid block components which have different molecular structures of recurring units from each other; thus, a polyimide - polyamic acid block copolymer having coexisting properties derived from each of the block components is produced. In this process, it is easy to sufficiently control the conditions for each polycondensation reaction, so that the polyimide - polyamic acid block copolymer having expected properties can be produced with certainty. By imidization, the polyimide - polyamic acid block copolymer becomes a polyimide block copolymer having coexisting excellent properties of each of the polyimide block components together; therefore, a polyimide having coexisting excellent plural properties from each of the block components such as the properties necessary for a liquid crystal alignment layer is obtained.

With the thin layer forming agent of this invention, as the major component polymer is a polyimide-type block copolymer comprised of plural kinds of polyimide block components bonded to each other, the inherent properties of each block element can coexist. Therefore, using this thin layer forming agent as a liquid crystal alignment layer forming agent, a liquid crystal alignment layer having excellent plural properties, which are difficult to obtain by conventional methods, can be obtained effectively and easily.

The liquid crystal alignment layer of this invention provides a liquid crystal display element of excellent performance with its coexisting plural properties that are unachievable in conventional methods.

With the process of producing the liquid crystal alignment layer of this invention, alignment property correction can be accomplished with high efficiency by irradiating, and thus excellent liquid crystal display elements can be produced.

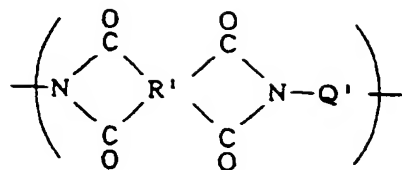
**Claims**

1. A process of producing a block copolymer type polyamic acid wherein a first polyamic acid block and a second polyamic acid block having a different structure from the first polyamic acid block are included in a molecule, the process comprising the following steps: obtaining a first polyamic acid prepolymer having amino groups at its ends by a reaction between a tetracarboxylic component and a diamine component, obtaining a second polyamic acid prepolymer having reactive groups originating from a tetracarboxylic component at its ends by a reaction between a tetracarboxylic component and a diamine component, and reacting the first polyamic acid prepolymer with the second polyamic acid prepolymer.

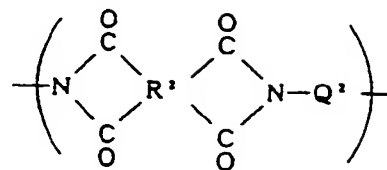
2. A process of producing a polyimide block copolymer; comprising the step of imidizing a block copolymer type polyamic acid produced by the process of Claim 1 to obtain a polyimide block copolymer comprising a first polyimide block and a second polyimide block in the molecule.
- 5 3. A process of producing a polyimide block copolymer wherein a first polyimide block and a second polyimide block having a different structure from the first polyimide block are included in a molecule, the process comprising the following steps:  
obtaining a first polyimide prepolymer having amino groups at its ends by a reaction between a tetracarboxylic component and a diamine component,  
10 obtaining a second polyimide prepolymer having reactive groups originating from a tetracarboxylic component at its ends by a reaction between a tetracarboxylic component and a diamine component, and  
reacting the first polyimide prepolymer with the second polyimide prepolymer.
- 15 4. A process of producing a polyimide block copolymer wherein a first polyimide block and a second polyimide block having a different structure from the first polyimide block are included in a molecule, the process comprising the following steps:  
obtaining a first polyimide prepolymer having isocyanate groups at its ends by a reaction between a tetracarboxylic dianhydride component and a diisocyanate component,  
obtaining a second polyimide prepolymer having carboxylic anhydride groups at its ends by a reaction between a  
20 tetracarboxylic dianhydride component and a diisocyanate component, and reacting the first polyimide prepolymer with the second polyimide prepolymer.
- 25 5. A process of producing a polyimide-polyamic acid block copolymer wherein a polyimide block and a polyamic acid block are included in a molecule, the process comprising the following steps:  
obtaining a polyimide prepolymer having carboxylic anhydride groups or isocyanate groups at its ends by a reaction between a tetracarboxylic dianhydride component and a diisocyanate component, obtaining a polyamic acid prepolymer having amino groups or carboxylic anhydride groups at its ends by a reaction between a tetracarboxylic  
30 dianhydride component and a diamine component, wherein a polyamic acid prepolymer having amino groups at its ends is used for the reaction when the polyimide prepolymer contains carboxylic anhydride groups at its ends and  
a polyamic acid prepolymer having carboxylic anhydride groups at its ends is used for the reaction when the polyimide prepolymer contains isocyanate groups at its ends.
- 35 6. A process of producing a polyimide-polyamic acid block copolymer wherein a polyimide block and a polyamic acid block are included in a molecule, the process comprising the following steps:  
obtaining a polyimide prepolymer having reactive groups originating from a tetracarboxylic component or amino groups at its ends by a reaction between a tetracarboxylic component and a diamine component,  
obtaining a polyamic acid prepolymer having amino groups or reactive groups originating from a tetracarboxylic component at its ends by a reaction between a tetracarboxylic component and a diamine component,  
40 wherein a polyamic acid prepolymer having amino groups at its ends is used for the reaction when the polyimide prepolymer contains reactive groups originating from a tetracarboxylic component at its ends,  
and a polyamic acid prepolymer having reactive groups originating from a tetracarboxylic component at its ends is used for the reaction when the polyimide prepolymer contains amino groups at its ends.
- 45 7. A thin layer forming agent comprising:  
a polyimide-type block copolymer, having a first polyimide-type block and a second polyamides type block that is bonded to the first polyimide-type block and has a different structure from the first polyimide-type block;  
the first polyimide-type block having recurring units illustrated in formula 1 or 2, and the second polyimide-type block having recurring units illustrated in formula 3 or 4



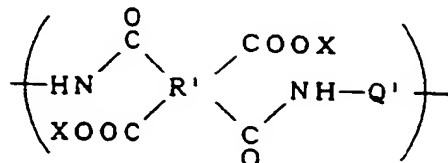
Formula 1



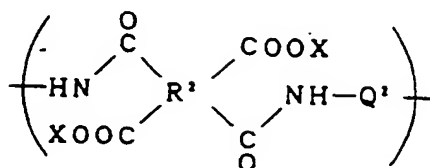
Formula 3



Formula 2



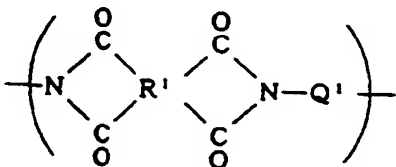
Formula 4



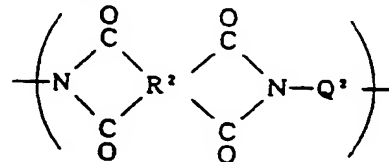
(wherein R<sup>1</sup> and R<sup>2</sup> are tetravalent organic groups which can be the same or different, Q<sup>1</sup> and Q<sup>2</sup> are divalent organic groups which can be the same or different, and X is a hydrogen atom or an organic group.)

8. A process of producing a liquid crystal alignment layer comprising the step of applying a liquid crystal alignment layer forming agent on to a substrate surface to form a thin layer and a step of aligning the thin layer; wherein the liquid crystal alignment layer forming agent contains a polyimide block copolymer soluble in organic solvent, having in the molecule a first polyimide-type block and a second polyimide-type block that is bonded to the first polyimide-type block and has a different structure from the first polyimide-type block, the first polyimide-type block having recurring units illustrated in formula 1 or 2, and the second polyimide-type block having recurring units illustrated in formula 3 or 4

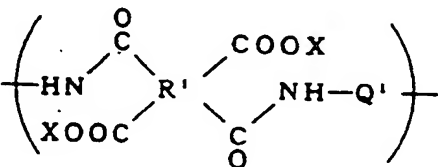
Formula 1



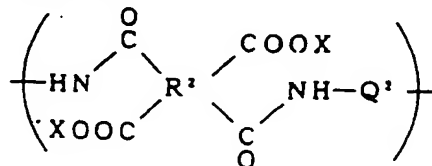
Formula 3



Formula 2



Formula 4



(wherein R<sup>1</sup> and R<sup>2</sup> are tetravalent organic groups which can be the same or different; Q<sup>1</sup> and Q<sup>2</sup> are divalent organic groups which can be the same or different, and X is a hydrogen atom or an organic group.)

9. A process according to claim 8 of producing a liquid crystal alignment layer, further comprising the steps of producing a thin layer of the polyimide-type block copolymer on a substrate surface and correcting alignment properties and aligning by irradiating at least a selected region of the thin layer.

10. A process according to claim 8 of producing a liquid crystal alignment layer, wherein the first polyimide-type block is a polyimide block having recurring units of formula 1 and the second polyimide-type block is a polyimide block having recurring units of formula 3.

11. A process according to claim 8 of producing a liquid crystal alignment layer, wherein the first polyimide-type block is a polyamic acid block having recurring units of formula 2 and the second polyimide-type block is a polyamic acid block having recurring units of formula 4.

12. A process according to claim 8 of producing a liquid crystal alignment, wherein the first polyimide-type block is a polyimide block having recurring units of formula 1 and the second polyimide-type block is a polyamic acid block having recurring units of formula 4.

13. A process according to claim 8 of producing a liquid crystal alignment layer wherein at least one of  $R^1$  of formula 1 or 2, or  $R^2$  of formula 3 or 4 is a residue of a cyclic aliphatic tetracarboxylic compound selected from the group consisted of tetracarboxylic acids, tetracarboxylic dianhydrides and tetracarboxylic esters.

14. A process according to claim 13 of producing a liquid crystal alignment layer, wherein at least one of  $R^1$  of formula 1 or 2, or  $R^2$  of formula 3 or 4 is a residue of a cyclic aliphatic tetracarboxylic dianhydride selected from the group consisting of:

2, 3, 5 - tricarboxycyclopentylacetic dianhydride;

1, 2, 3, 4 - cyclobutanetetracarboxylic dianhydride;

1, 3 - dimethyl - 1, 2, 3, 4 - cyclobutanetetracarboxylic dianhydride;

1, 3, 3a, 4, 5, 9b - hexahydro - 5 - (tetrahydro - 2, 5 - dioxo - 3 furanyl) naphtho [1, 2 - c] furan - 1, 3 - dione;

1, 3, 3a, 4, 5, 9b - hexahydro - 5 - methyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) naphtho [1, 2 - c] furan - 1, 3 - dione;

1, 3, 3a, 4, 5, 9b - hexahydro - 5 - methyl - 5 - (tetrahydro 2, 5 - dioxo - 3 - furanyl) naphtho [1, 2 - c] furan - 1, 3 - dione;

1, 3, 3a, 4, 5, 9b - hexahydro - 7 - methyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) naphtho [1, 2 - c] furan - 1, 3 - dione;

1, 3, 3a, 4, 5, 9b - hexahydro - 7 - ethyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) naphtho [1, 2 - c] furan - 1, 3 - dione;

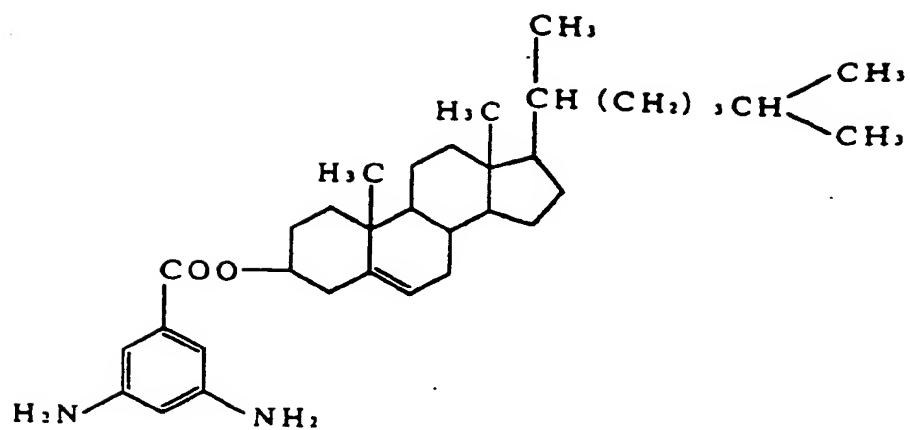
1, 3, 3a, 4, 5, 9b - hexahydro - 8 - methyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) naphtho [1, 2 - c] furan - 1, 3 - dione; and

1, 3, 3a, 4, 5, 9b - hexahydro - 8 - ethyl - 5 - (tetrahydro - 2, 5 - dioxo - 3 - furanyl) naphtho [1, 2 - c] furan - 1, 3 - dione.

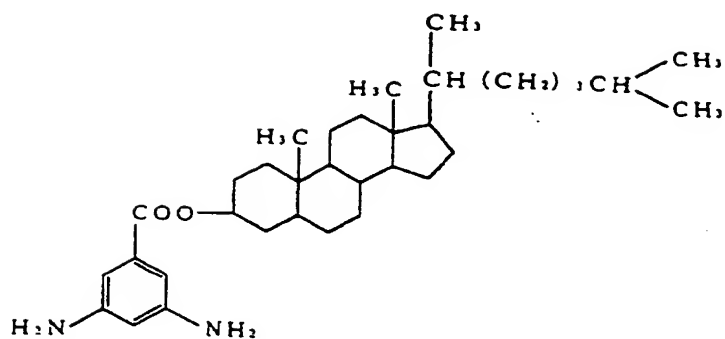
15. A process according to claim 8 of producing a liquid crystal alignment layer, wherein  $Q^1$  of formula 1 or 2 is a residue of an aromatic diamine compound having two amino groups ( -  $NH_2$  ) bonded to an aromatic ring, and having heteroatoms other than the nitrogen atoms of the amino groups, and  $Q^2$  of formula 3 or 4 is a residue of an aromatic diamine compound having two amino groups bonded to an aromatic ring, and having no heteroatoms other than the nitrogen atoms of the amino groups.

16. A process according to claim 15 of producing a liquid crystal alignment layer, wherein  $Q^1$  of formula 1 or 2 is a residue of a diamine compound selected from the group consisting of component A01 to A14:

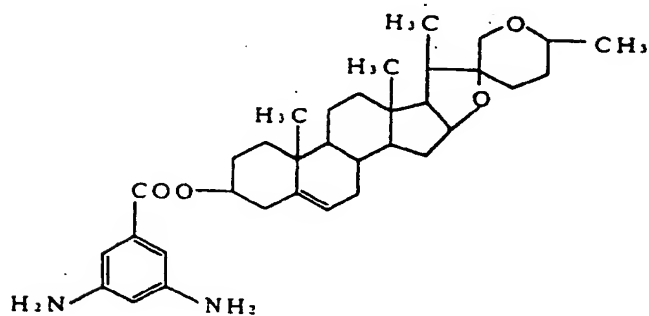
A01



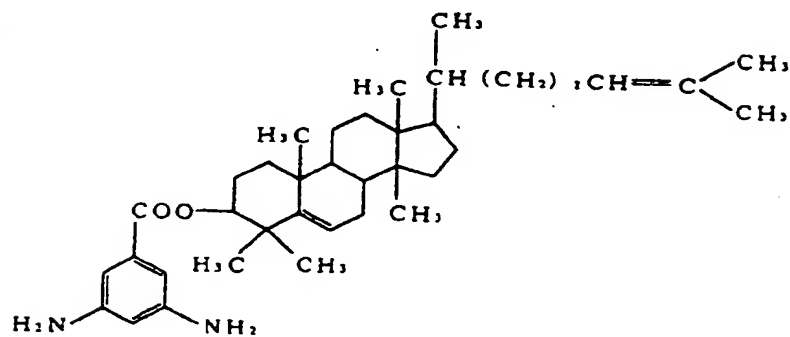
A02



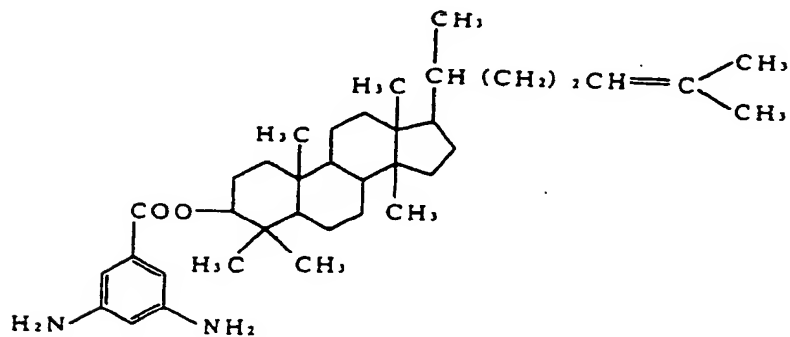
A03



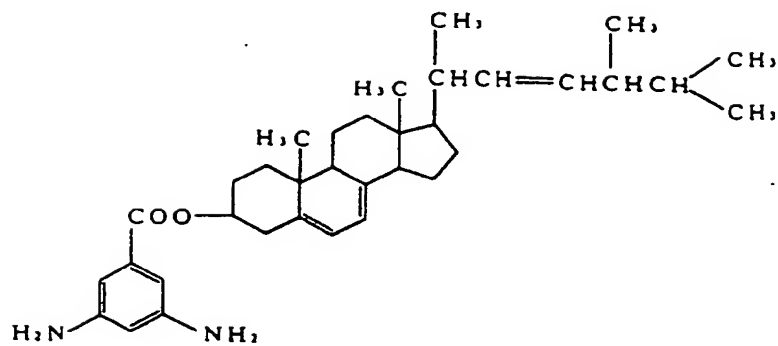
A04



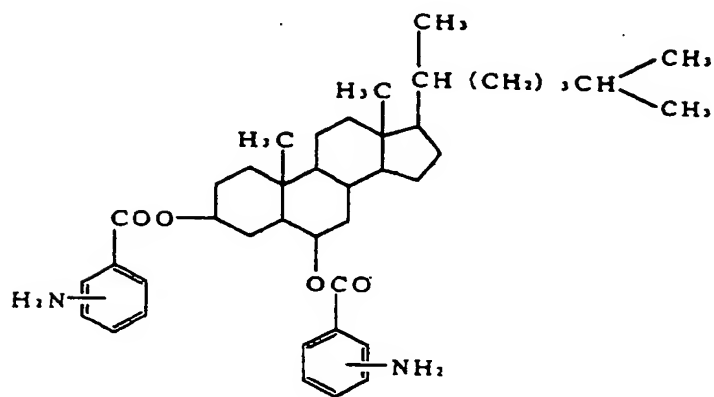
A05



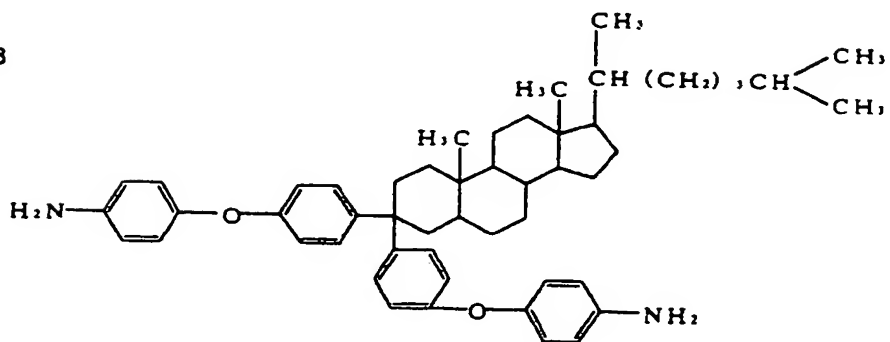
A06



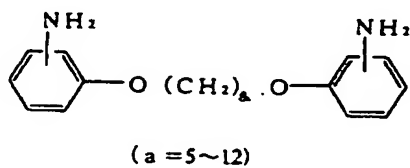
A07



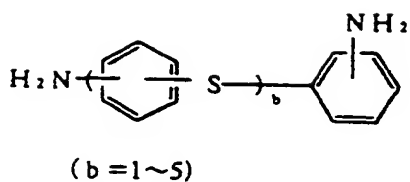
A08



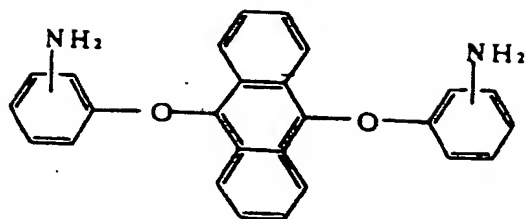
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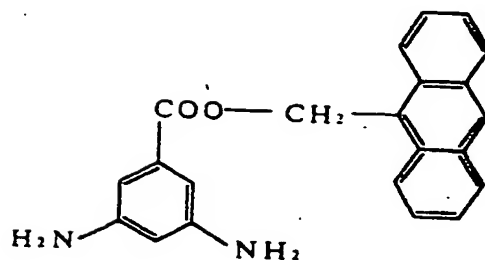
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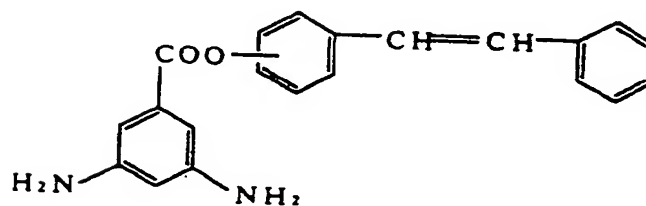
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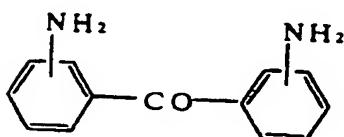
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A13



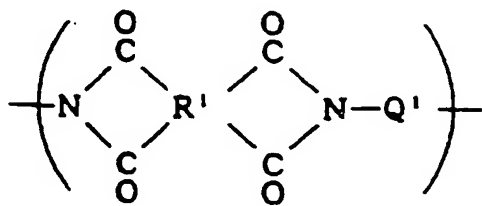
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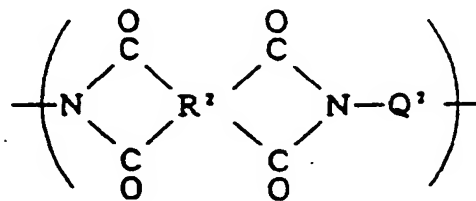
17. A liquid crystal alignment layer characterised by having a polyimide block copolymer comprising, in a molecule, a first polyimide block and a second polyimide block which is bonded to the first polyimide-type block and has a different structure from the first polyimide block,

the first polyimide block having recurring units illustrated in formula 1 and the second polyimide block having recurring units illustrated in formula 3:

Formula 1



Formula 3



wherein:

R<sup>1</sup> and R<sup>2</sup> are tetravalent organic groups which can be the same or different.

(19)



Europäisches Patentamt

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(11)

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(71) Applicant: JAPAN SYNTHETIC RUBBER CO., LTD.

Tokyo 104 (JP)

(72) Inventors:

• Miyamoto, Tsuyoshi  
Yokohama-shi (JP)

• Kimura, Masayuki

Yokkaichi-shi (JP)

• Eguchi, Kazuhiro,

Tsuchiura Reikusaide Haitzu 511

Tsuchiura-shi (JP)

• Matsuki, Yasuo

Yokkaichi-shi (JP)

(74) Representative: Lamb, Martin John Carstairs

MARKS & CLERK,

57-60 Lincoln's Inn Fields

London WC2A 3LS (GB)

(54) **A process of producing a polyimide block copolymer**

(57) A polyamide-type copolymer, a process of producing the same and use of the same in a thin layer forming agent.

In order to provide a polyamide-type copolymer suitable for producing an alignment layer in an SBE type display element with high transparency, adhesion, pretilt angle etc, the present invention provides processes of producing a block copolymer type polyamic acid, a polyimide block copolymer, a polyimide-polyamic acid block copolymer and a liquid crystal alignment layer wherein, in separate steps, first and second prepolymers comprising polyamic acid prepolymers or polyamide prepolymers are prepared and subsequently reacted together, and if necessary, imidised.

The invention also provides a thin layer forming agent having a first polyimide-type block and a second polyimide-type block bonded to the first polyimide-type block and having a different structure from the first polyimide type block.

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## EUROPEAN SEARCH REPORT

Application Number  
EP 96 30 0662

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 479 148 A (E.I. DUPONT DE NEMOURS AND COMPANY) * claim 8 *	1-3,6	G02F1/1337 C08G73/10
X	EP 0 337 355 A (NISSAN CHEMICALS INDUSTRIES LIMITED) * page 3, line 1-4; claims 1-5 *	1-3, 6-13,17	
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A	EP 0 540 829 A (NISSAN CHEMICALS INDUSTRIES LIMITED) * claims 3-5 *	1,14,16	
A	EP 0 400 635 A (CANON KABUSHIKI KAISHA) * claims 3-12 *	1,14-16	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C08G G02F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 April 1997	Examiner Glanddier, A
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

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